in reactions which use superoxide radicals as precursors.[16,17] Metal ions are strongly implicated in these reactions and there is evidence that superoxide radicals form metastable complexes with metal ions[32-34] which might then participate in a Haber-Weiss type reaction.

Alternatively, the superoxide radical can serve as a source of hydroxyl radicals by reducing Fe(III), thus permitting a Fenton reactions:[20]

$$O_2^- + Fe(III) \rightarrow Fe(II) + O_2 \qquad (12)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH + OH^- \qquad (1)$$

That Fenton-type reactions can occur even with complexed metal ions, e.g., ferric ethylenediaminetetraacetate, has already been demonstrated.[19,35] Thus the present status is that unless some very convincing evidence is produced in favor of singlet molecular oxygen ($^1O_2$, a species also in high fashion),[17,36] accumulating evidence is tipping the scales in the direction of the "Walling concepts"[18] of metal catalysis.

Acknowledgments. The authors wish to thank Drs. H. A. Schwarz and A. O. Allen for their constructive criticism and many helpful suggestions.

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(1) Research carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported in part by its Division of Basic Energy Sciences and NIH Grant 1 RO1 GM 23656-01.
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A Coordination Chemistry Study of a Nickel Surface. The Chemistry of Ni(111) with Triply Bonded Molecules

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Abstract: The chemistry of the (111) surface of nickel has been investigated for a series of molecules with unsaturated bonds: acetonitrile, methyl isocyanide, cyanogen, acetylene, 2-butyne, carbon monoxide, and ethylene. Acetonitrile, as in coordination chemistry, was weakly bound to the nickel surface and was readily and completely displaced by carbon monoxide at 300 K. This nitrile formed a simple ordered surface structure at 300 K; the observed (2 × 2) unit cell would accommodate acetonitrile molecules, normal to the surface, on every other nickel atom. The isomeric methyl isocyanide molecule was strongly bound to the surface, was not reversibly desorbed on temperature increase, and was not displaced by carbon monoxide. Dehydrogenation of the isocyanide occurred at ~380 K and above 800 K N_2 evolved to leave only carbon on the nickel crystal surface. Cyanogen was also strongly chemisorbed: thermal desorption gave N_2 at ~800 K in contrast to platinum surfaces which reversibly desorb cyanogen. Cyanogen on the Ni(111) surface formed an extremely stable, ordered (6 × 6) structure at ~400 K. Acetylene, 2-butyne, and ethylene were irreversibly chemisorbed on the nickel surface.

Introduction

Although a clean metal surface has absolutely no analogue in coordination chemistry,[4] metal surfaces with monolayers of chemisorbed molecules may have close analogues within coordination chemistry—mononuclear complexes, dinuclear compounds, and discrete molecular metal clusters. Experimental evidence qualitatively supports the analogy.[6-9] However, despite the diversity of supportive data, the evidence is

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insufficient to provide *critical* tests of the analogy.[10] At this stage of understanding, it may be most constructive to seek areas where the analogy may break down, and this is the issue addressed by our research.[10]

We describe here our initial studies of a nickel surface which parallels earlier studies of the coordination chemistry of nickel complexes, especially cluster compounds[12-15] with ligands that have triple bonds. The potential range of bonding modes for molecules with triple bonds is large[16] and this potential diversity should provide an excellent opportunity for detecting significant differences between surfaces and coordination complexes.

We elected to begin this study by examining the crystal face chemistry[14] of nickel under ultrahigh-vacuum conditions so as to provide a well-characterized initial reference point. Described below is the chemistry of molecules with triple bonds—nitriles, isocyanides, cyanogen, acetylenes, and carbon monoxide—at the (111) crystal face of nickel. This nickel crystal face, the least analogous to a metal cluster, was selected for experimental simplicity because it is the most thermodynamically stable one and has only two types of surface atom sites which differ only because of the subsurface layer packing in a cubic close packed structure. In this study, displacement and thermal desorption or dissociation reactions,[17-19] both effective probes in coordination studies, have been extensively employed.

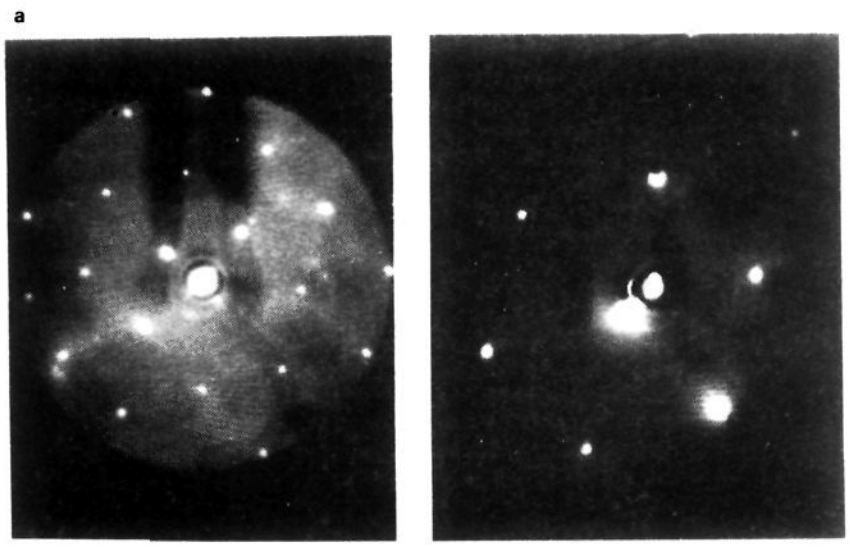
Experimental Section

Reagent grade acetonitrile was used directly and also after distillation from CaH_2; there was no distinguishable difference between the surface chemistry of the nitrile derived from these two sources. Methyl isocyanide was prepared by a standard literature procedure, fractionally distilled, and stored under vacuum at near liquid nitrogen temperature. Commercial acetylene was slowly passed through molecular sieve that was externally cooled to −78.5 °C. Ethylene and cyanogen (>99% purity) from Matheson were used without further purification. 2-Butyne was obtained from Chemical Samples Co. (99.8%). Liquids were thoroughly degassed prior to use. All these reagents showed no detectable impurities in mass spectral analysis.

Experiments were conducted in a Varian surface analysis ultrahigh-vacuum chamber equipped with low-energy electron diffraction and Auger electron spectroscopy capabilities. The base pressure of the system was approximately 2×10^{-9} Torr. The system was also equipped with a quadrupole mass filter for residual gas analysis and monitoring of the products from displacement and thermal desorption experiments. The gases were admitted to the chamber through a leak valve with a hypodermic needle attached; the needle tip typically was positioned within 1–2 mm of the crystal so that most molecules admitted through the needle struck the crystal surface, thus minimizing chamber wall contamination.

The nickel crystal was oriented by X-ray Laue and then mechanically polished using 0.05-μm alumina for the last polishing stage. After the polishing, the orientation was again checked and was found to be the (111) plane within the accuracy of the Laue apparatus (0.5°). The crystal was then placed in the chamber. The main surface impurities were sulfur and carbon as determined by Auger electron spectroscopy. The sulfur was easily removed by cycles of Ar-ion sputtering at a crystal temperature of 1100 K followed by annealing at the same temperature under vacuum. The sputtering was done with 300-V Ar ions. The carbon was removed by sputtering the crystal at ~650 K with 300-V Ar ions. This lower temperature sputtering was used to remove the carbon since carbon is quite mobile and dissolves in the bulk of the crystal at higher temperatures and quickly segregates to the surface as the crystal is cooled. Following the carbon removal, the crystal was annealed at 1100 K for at least 1 h. After the cleaning procedure, Auger analysis showed little or no impurities (C <5% monolayer and S <1% monolayer) and the low-energy electron diffraction pattern showed the pseudohexagonal pattern of Ni(111) with sharp spots and very low background.

Results



CH_3CN on Ni(111) CLEAN Ni(111)

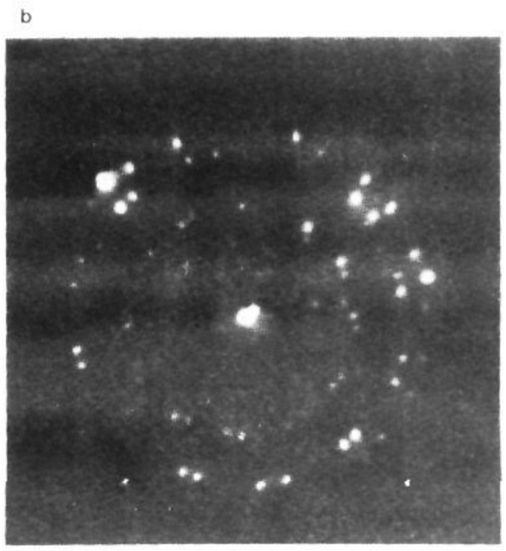


Figure 1. (a) Photograph of the (2 × 2) low energy electron diffraction pattern obtained from ordered CH_3CN on Ni(111) next to the diffraction pattern obtained from clean Ni(111). Voltage is 100 V. (b) Photograph of the LEED pattern obtained by heating CH_3CN on Ni(111) to ~400 K.

Acetonitrile chemisorbed at 300 K on the Ni(111) crystal face at exposures of 10^{-8}–10^{-6} Torr s to yield a well-ordered (2 × 2) surface structure which was very electron beam sensitive; partial disordering and possibly desorption occurred within minutes upon exposure to the low-energy electron beam. By lowering the crystal temperature to about 285 K, the lifetime of the ordered state was increased, and in Figure 1a is a photograph of a well-defined (2 × 2) low-energy electron diffraction pattern obtained under these conditions. For this ordered state, the Auger electron spectrum showed both carbon and nitrogen to be present at or near the surface with respective peak to peak intensity ratio of ~2:1 after adjustment for the relative sensitivities (1.5:1) of Auger electron spectroscopy to carbon and nitrogen.

Acetonitrile chemisorption was thermally reversible but was not quantitative. Thermal desorption with a temperature gradient of 16 K per second gave desorption of about one-half of the acetonitrile at 360 K as established by the Auger spectrum taken after the crystal was allowed to cool back to 300 K. Assuming a first-order desorption process, the thermal desorption data (see Figure 2) indicate a desorption activation energy of about 20 kcal/mol. In thermal desorption experiments in which the maximum crystal temperature was 900 K, there was in addition to the CH_3CN desorption at 360 K a nitrogen (N_2) desorption peak at 800 K. At this point, Auger analysis (300 K) showed no nitrogen and very little carbon remaining on the surface; the residual carbon was largely in the bulk phase. The (2 × 2) acetonitrile surface structure obtained at 300 K converted at 400 K (upon removal of one-half of the CH_3CN) to a new and complex surface structure shown in Figure 1b. This new surface structure, which contained both carbon and nitrogen at a normalized ratio of 2:1 (Auger analysis), was not beam sensitive and was stable up to 800 K,

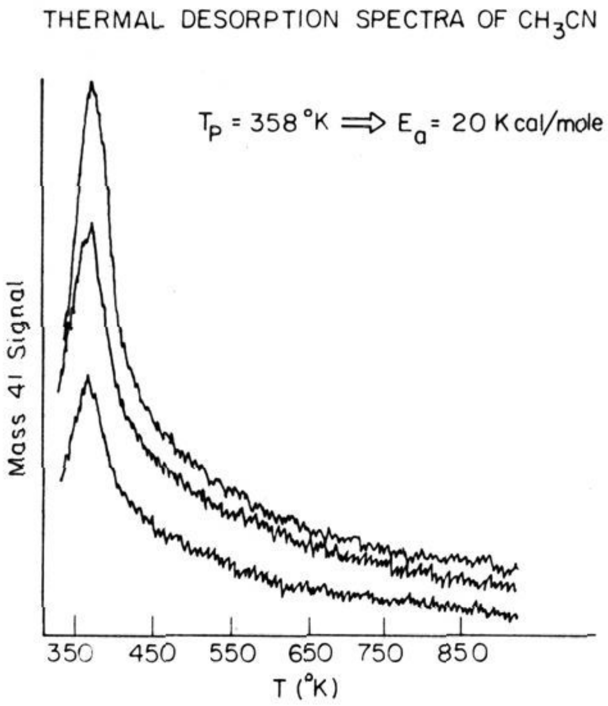


Figure 2. Thermal desorption spectra from CH_3CN on Ni(111). The three curves correspond to three different initial coverages.

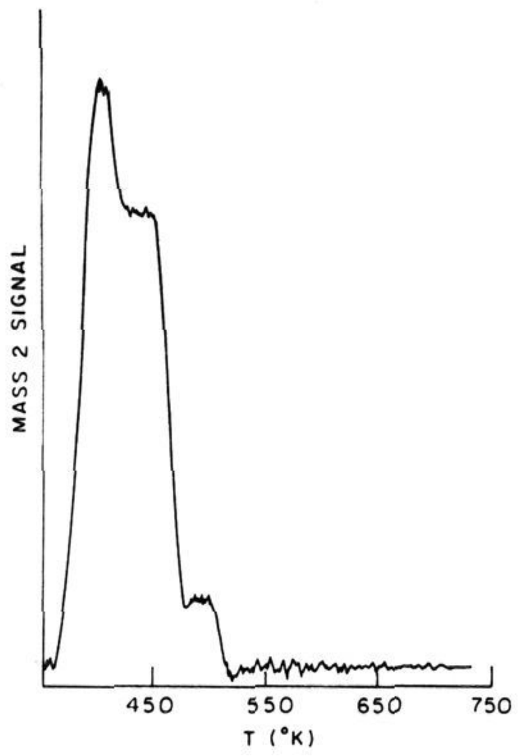
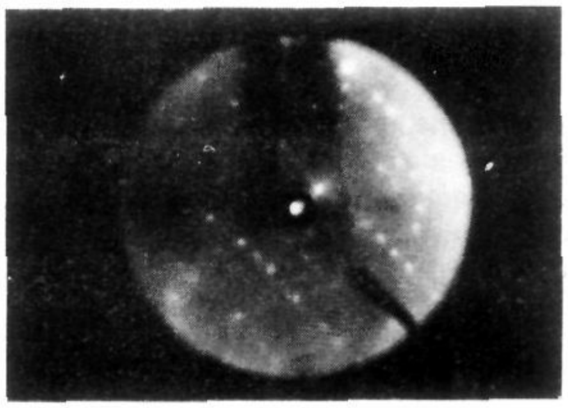


Figure 3. Thermal desorption spectra monitoring mass 2 (H_2) from CH_3NC on Ni(111).

Figure 4. Photograph of the LEED pattern obtained by heating CH_3NC to ~375 K. The ring of split spots around the (0,0) beam are ¼ order diffraction spots. The dark circle is from the glow of the electron gun.



C_2N_2 on Ni(111)

CLEAN Ni (111)

Figure 5. Top: photograph of the (6 × 6) LEED pattern obtained by heating the C_2N_2 adsorbed on Ni(111) to 400 K. Bottom: photograph of the LEED pattern from clean Ni(111); voltage is 125 V.

where decomposition occurred with N_2 evolution (mass spectrometric analysis).

Exposure of the Ni(111)-(2 × 2)-CH_3CN surface structure to carbon monoxide at 300 K led to complete acetonitrile displacement. This reaction was monitored by mass spectrometry, where as soon as CO was sensed the 41 peak of acetonitrile appeared and increased with time. Auger analysis quantitatively delineated the process by the decline and disappearance of the 381-eV nitrogen peak and the growth of the 515-eV oxygen peak.

Adsorption of CH_3NC at 300 K at exposures of 10^{-8}–10^{-6} Torr s produced an immediate high background intensity on the fluorescent LEED screen; there was no ordering and the sticking coefficient was close to unity. The normalized carbon and nitrogen (Auger) peak to peak intensity ratio was 2:1. A flash heating of the crystal (16 K/s) did not yield detectable amounts of mass 41, either CH_3NC or CH_3CN, but did yield hydrogen (H_2) at 375 K and above. There were three distinguishable thermal desorption peaks of H_2 indicating decomposition of the molecular adsorbate (Figure 3). Coincident with the initial removal of H_2 at 375 K, a well-ordered surface structure formed (Figure 4), that was stable at temperatures up to ~450 K. Additional H_2 evolved at 450 K (see Figure 3) and the adsorbate became disordered and remained disordered up to 800 K, where N_2 desorption was observed. The disordered adsorbate obtained at 300 K and the ordered adsorbate obtained at ~380 K showed no evidence for interaction with the electron beam, unlike molecularly adsorbed CH_3CN. Exposure of the disordered adsorbate obtained at 300 K or of the ordered surface structure to CO at 10^{-6} Torr did not result in displacement of the adsorbate.

Adsorption of cyanogen at 300 K at exposures of 10^{-8}–10^{-6} Torr s produced a disordered surface structure with a normalized carbon to nitrogen peak to peak intensity ratio of ~0.9:1. Thermal desorption produced only N_2 evolution at 800 K; desorption of C_2N_2 or CN was not detected. On heating to 400 K, a (6 × 6) surface structure formed (Figure 5); the carbon coverage was ~0.3 monolayer. This was a stable surface structure that withstood temperatures up to 800 K, where the desorption of N_2 became detectable. Exposure of the disordered adsorbate obtained at 300 K or of the (6 × 6) surface structure to carbon monoxide did not result in displacement of any mass spectrometrically detectable species or cause any change in the surface order.

Exposure of the clean Ni(111) surface to acetylene at 10^{-8} Torr s and 300 K produced a (2 × 2), electron beam sensitive surface structure shown in Figure 6a. Overexposure to C_2H_2 caused the diffraction pattern to become streaky, then ring-like (Figure 6b), and finally there was complete disordering as indicated by the high background intensity on the fluorescent LEED screen and the absence of all extra diffraction features. This same disordering phenomena occurred with time at 300 K. On heating the chemisorbed acetylene surface, only H_2 desorption was detected.

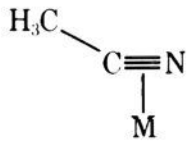
Ethylene chemisorbed on the Ni(111) surface at 300 K without ordering and only H_2 desorption was spectrometrically observed on heating. Dimethylacetylene adsorption at 300 K and at exposures of 10^{-8}–10^{-6} Torr s yielded a poorly ordered $(\sqrt{3} \times \sqrt{3})$ R30° surface structure that resisted attempts to achieve better ordering by changing either exposure or surface temperature and that yielded only H_2 desorption on heating.

Discussion

In coordination chemistry, acetonitrile is a weak donor and acceptor that binds through the nitrogen atom in a near linear array, **1**.[20] Side bonding, **2**, has been proposed, but is not documented by crystallographic studies for simple alkyl nitriles.[20] Possible alternative bonding modes in dinuclear or cluster complexes or on metal surfaces are those of **3** and **4** where there is extensive rehybridization of the carbon and nitrogen orbitals; analogous acetylene[23,24] and alkyl isocyanide[25] complexes are known.

$H_3C{-}C{\equiv}N{-}M$

1



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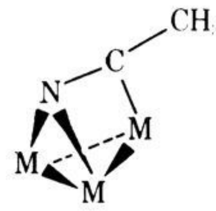

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Our nickel surface studies clearly demonstrate that acetonitrile is very weakly bound to the nickel(111) face. The activation energy for thermal desorption is only 20 kcal/mol and the chemisorbed acetonitrile is readily and quantitatively displaced by carbon monoxide, whose activation energy for thermal desorption is ~26 kcal/mol. These data are fully consistent with established coordination chemistry for a binding mode like **1** with acetonitrile normal to the surface.[26] The ordered (2 × 2) structure observed for acetonitrile on the nickel(111) face does not qualitatively provide any information, although it is notable that a relatively close-packed array of acetonitrile molecules (using the van der Waals radii and allowing for some thermal motion of the atoms in CH_3CN) could generate a (2 × 2) structure.

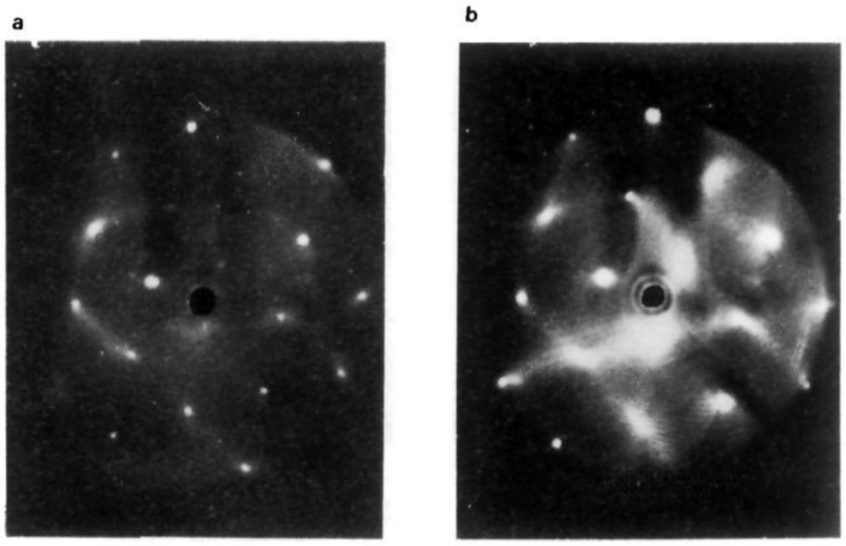
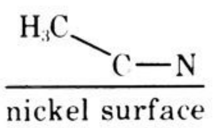


Figure 6. (a) Photograph of the (2 × 2) LEED pattern obtained from C_2H_2 on Ni(111). (b) Photograph of the (2 × 2)-C_2H_2 LEED pattern after ~2 min.

In sharp contrast to acetonitrile, methyl isocyanide was strongly chemisorbed on the Ni(111) surface and thus clearly did not rearrange to the more thermodynamically stable isomer, acetonitrile. The sticking coefficient of the isocyanide was close to one, whereas the value for the nitrile was quite low. Furthermore, chemisorbed methyl isocyanide was not displaced by carbon monoxide. Since there was no ordered phase on chemisorption at 300 K, the low-energy electron diffraction experiment provided no information. To this point, the displacement chemistry is fully consistent with the ordering of ligand field strengths in coordination chemistry with $CH_3NC > CO > CH_3CN$. On warming the methyl isocyanide surface structure, no CH_3NC or CH_3CN was detected by mass spectrometry; hydrogen loss was the only low-temperature process detected and three discrete hydrogen maxima were mass spectrally observed in the temperature range of 375–480 K. Nitrogen (N_2) desorption was detected at 800 K. We suggest that the isocyanide is initially bound to the surface through the carbon and nitrogen atoms in a fashion formally analogous to that observed for isocyanides in nickel clusters[25] so as to place the methyl group proximal to the surface **5**. Facile scission of carbon–hydrogen bonds in the ligands of coordinately unsaturated transition metal complexes is a relatively common phenomenon when a ligand carbon–hydrogen bond can closely approach the metal atom.[27,28] The ordered and stable surface structure that results from the hydrogen loss is large enough to accommodate a CNC plane parallel to the metal surface. Note that chemisorbed CH_3CN, proposed to be more or less normal to the surface, largely underwent a molecular thermal desorption and only a fraction of the CH_3CN molecules underwent dehydrogenation.



5

Cyanogen oxidatively adds to a metal center in metal coordination complexes so as to raise the formal oxidation state of the metal by two and form two metal–cyanide bonds as demonstrated[29] for a metal in the platinum group, **6**.

$$Pt(PR_3)_3 + NCCN \rightarrow Pt(PR_3)_2(CN)_2$$

6

Hence it would seem reasonable to expect a dissociative chemisorption for cyanogen, at least for the more electropositive metals. Cyanogen adsorbed strongly on the nickel(111) face at 300 K. Carbon monoxide did not displace the cyanogen at 300 K. The surface structure was not ordered but at 400 K a well-defined (6 × 6) structure formed which was thermally stable to 800 K and was insensitive to the electron beam. We presume that dissociative chemisorption initially prevailed. The CN group could be normal or parallel to the surface; if the former occurred there would be a high probability of an ordered structure with a small unit cell, e.g., a (2 × 2) structure. With the relatively electropositive nickel, we suggest that the CN group is more or less parallel to the surface with both the carbon and nitrogen atoms bonded to the surface.[30] The ordering of the surface structure that occurred at 400 K might

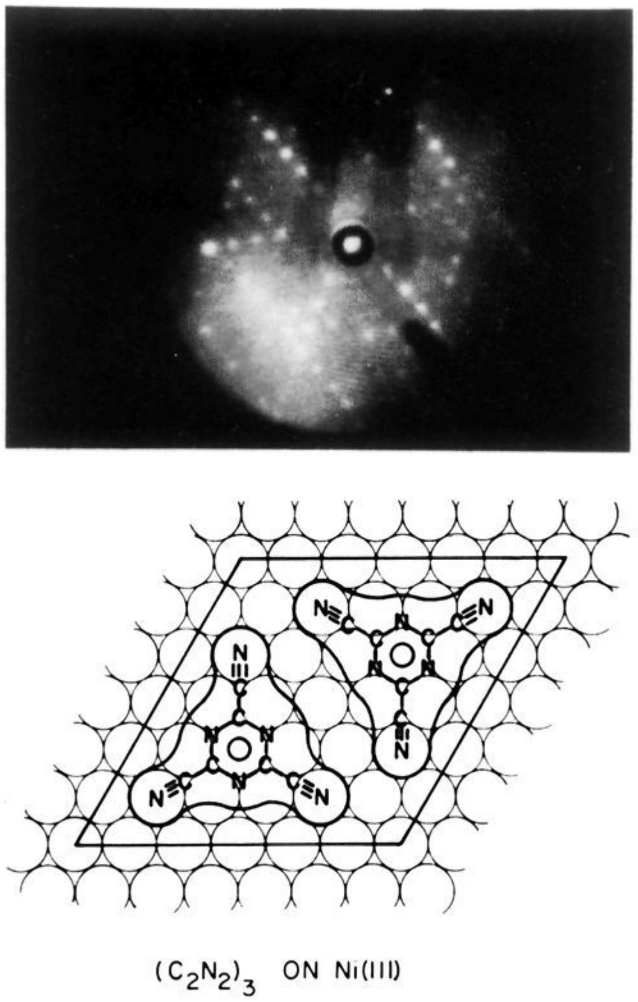
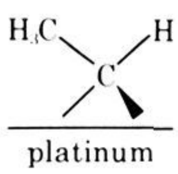


Figure 7. Top: photograph of the (6 × 6) LEED pattern from C_2N_2 on Ni(111) after heating to 400 K. Bottom: possible ordering of the trimer of C_2N_2 in the (6 × 6) unit cell of the surface structure.

result from a polymerization of the cyanide groups; a tricyanotriazine unit (a trimer of C_2N_2) would neatly generate a (6 × 6) unit cell (Figure 7).[31a] Decomposition of the surface structure at ~800 K led to complete removal of nitrogen whereas initial studies of bulk $Ni(CN)_2$ decomposition showed nitrogen and cyanogen to be formed from 700 to 900 K.[31b] This is in sharp contrast to cyanogen on Pt(100) and Pt(110), which reversibly yielded cyanogen and CN radical at elevated temperatures.[32] Perhaps cyanogen chemisorbed on other nickel faces will show cyanogen formation at elevated temperatures.

In the chemisorption of ethylene, acetylene, and 2-butyne, the *initial* interaction should be with the hydrocarbon π system as conventionally observed for olefins and acetylenes in mononuclear metal complexes (Dewar-Chatt-Duncanson model)[33,34] and the secondary interaction should be multicenter as often found[23,24] for acetylenes in dinuclear or cluster complexes (analogues of **3** and **4**). However, in each case this would place the carbon-hydrogen bonds close to the nickel surface. Scission of these bonds should occur readily either at 300 K or slightly above. In fact, we found all three hydrocarbons to chemisorb irreversibly; on raising the surface temperature, only hydrogen was evolved. Qualitative observations on the rate of organic adsorbate buildup indicated the order of the sticking coefficients to be $HC{\equiv}CH > H_2C{=}CH_2 \geq CH_3C{\equiv}CCH_3$, an ordering that follows the complexation ordering in mononuclear coordination complexes.

Acetylene adsorbed strongly on the Ni(111) surface to form a (2 × 2) surface structure that disordered rapidly upon further exposure to C_2H_2 or slowly under vacuum at 300 K. This chemisorption behavior can be compared to that of C_2H_2 on the Pt(111) surface where a (2 × 2) surface structure formed[35] and then disordered on increased exposure but was stable under vacuum at 300 K. Ethylene did not form an ordered surface structure at 300 K. If this hydrocarbon chemisorption behavior correlates with that on Pt(111), C_2H_2 and C_2H_4 would form the same species in the *disordered* layer. Demuth has studied the chemisorption of C_2H_2 on the Ni(111) surface by LEED and photoemission and reported a (2 × 2) structure with "diffuse" spots followed by "streaking" at higher exposures.[36] This is similar to what we found (see Figure 6b). We do note, however, that the formation of streaks in the LEED pattern and the eventual disordering occurred slowly without further exposure to acetylene and with the LEED electron beam off. Acetylene on Pt(111) showed a similar structural change which was followed by changes in the intensities of the low-energy electron diffraction beams.[35] The second, more strongly bound, C_2H_2 phase on Pt(111) is presently thought to be a $HC\text{-}CH_3$,[37] **7**, or $C\text{-}CH_3$,[38] **8**, species which has picked up



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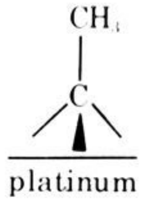

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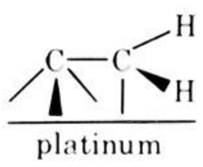

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hydrogen from the background.[37] A possible intermediate in the formation of this species is a CCH_2 species, **9**. It is possible that the transformation which we observe for C_2H_2 on Ni(111) is to a species similar to those observed for C_2H_2 on Pt(111).

2-Butyne produced a poorly ordered $(\sqrt{3} \times \sqrt{3})$ R30° surface structure upon adsorption on Ni(111) at 300 K and there was no transformation to a second phase as with C_2H_2. This internal olefin is probably bound to the surface in a different fashion than C_2H_2. Hydrogen migration and hydrogenation should be more difficult for 2-butyne. These data lend some credence to the suggestion that the C_2H_2 transformation is initially by a hydrogen transfer to form CCH_2 followed by hydrogenation with hydrogen from the background. The CCH_2 species has a precedent in metal cluster chemistry,[39] $H_2Os_3(CO)_9(CCH_2)$.

Carbon monoxide and hydrogen chemisorption were studied using the above techniques with results identical with those reported by Ertl[40] and Demuth.[41] The desorption temperature of carbon monoxide was 440 K in agreement with Ertl's finding. The desorption activation energy was 26 kcal/mol.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. We are also grateful to the National Science Foundation for fellowship support (J.C.H.) and the Hitchcock fund for lecturer support (E.L.M.).

References and Notes

(1) National Science Foundation Postdoctoral Fellow.
(2) Hitchcock Lecturer, 1977.
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(4) Reactivity is exceptionally high, the surface is truly heterogeneous, there are many potential binding sites differentiated by structure and reactivity level, and there are no ligands to sterically block sites or moderate reactivity. A clean metal surface can cleave carbon-hydrogen and carbon-carbon bonds with facility and can even cleave the extremely strong triple bonds of the nitrogen and carbon monoxide molecules. All these reactions may proceed at room temperature or below.[5] There is no parallel in molecular chemistry.
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comparable conditions—i.e., the same metal, molecule or molecules, and temperature—so as to have a more precise and incisive test of the analogy.
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Structure of the Iron-Containing Core in Ferritin by the Extended X-ray Absorption Fine Structure Technique

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Abstract: Extended X-ray absorption fine structure (EXAFS) measurements are used to determine the structure of the iron-containing core of ferritin. By comparing the EXAFS from ferritin with that from an Fe-glycine model compound, it is found that at room temperature the irons are surrounded by 6.4 ± 0.6 oxygens at 1.95 ± 0.02 Å which are likely in a distorted octahedral arrangement. Each iron also has 7 ± 1 iron neighbors at an average distance of 3.29 ± 0.05 Å. Considerable structural disorder was found which increased when the ferritin solution was frozen, indicating a possible phase transition occurring at lower temperatures. Combining these results with the known stoichiometry and density it is shown that the structure for the iron core is a layered arrangement with the iron in the interstices between two nearly close-packed layers of oxygens with approximate sixfold rotational symmetry, and that these compact O-Fe-O layers are only weakly bound to adjacent layers. The known phosphorus component is accounted for by terminating the layer into a strip whose width naturally explains the size of the core. The ferritin core consists, in this picture, of a strip folded back and forth upon itself in the form of a pleat. Measurements are also presented for two forms of the polymer of Spiro and Saltman, and it is found that only one form is possibly similar to ferritin.

I. Introduction

Iron is stored in animal tissue in two forms, ferritin and haemosiderin. Of the two, the nature and role of ferritin are the better understood.[2] Ferritin is a water-soluble protein which consists of an inorganic $(FeOOH)_8(FeO{\cdot}OPO_3H_2)$ micellar core[3,4] approximately 70 Å in diameter surrounded by an organic "shell", with a total diameter of ~120 Å.[5,6] When the protein is "full" of iron it has a molecular weight of approximately 900 000 which is nearly equally divided between the outer sheath and the micellar core. The iron in the core is known to be trivalent.[7]

Magnetic susceptibility and Mössbauer spectroscopic measurements[7,8] have shown conclusively that the Fe^{3+} ions in ferritin are exchange coupled, giving rise to superparamagnetic behavior. This, along with the stoichiometry, has led to the postulation that the Fe^{3+} ions in ferritin are connected by O^{2-} and OH^- bridges.[9,10]

Based upon X-ray diffraction patterns of horse spleen haemosiderin, Schwietzer[11] suggested that the iron core of this protein has the γ-FeOOH structure. Wöhler[12] and Fischbach et al.[13] have found, however, that if the ferritin or haemosiderin solid is isolated at room temperature, there is no trace of either α- or γ-FeOOH and that the early report of Schwietzer was an artifact of the method of preparation.

Utilizing low-angle X-ray scattering data obtained on iron-containing polymers, Brady et al.[14] have suggested that

0002-7863/79/1501-0067$01.00/0