X-Ray Photoelectron Spectroscopic Study of the Adsorption of Benzene, Pyridine, Aniline, and Nitrobenzene on Evaporated Nickel and Iron

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The adsorbed states of benzene, pyridine, aniline, and nitrobenzene on evaporated nickel and iron films have been investigated by X-ray photoelectron spectroscopy. Benzene adsorbed on the metals with π-d bonding exhibits a C 1s peak whose binding energy is lower by 0.8 eV on nickel and by 0.5 eV on iron than that for condensed benzene. Pyridine is also considered to chemisorb on the metal surfaces by π-d interaction as inferred from the low binding energy of the C 1s and N 1s electrons and from substitution reaction data with acetic acid. Aniline gives both a molecularly adsorbed species and an anion formed by release of a proton from the amine group. Nitrobenzene dissociates stepwise to give adsorbed nitrosobenzene with N 1s at 400.0 eV and an anion with N 1s at 397.6 eV which has released two oxygen atoms, forming surface oxygen. On the metal surfaces preoxidized by oxygen, pyridine and aniline bond to the surface through nitrogen lone pair electrons and their C 1s and N 1s electrons have virtually the same binding energies as those for condensed pyridine and aniline. Nitrosobenzene is a predominant species on the preoxidized surfaces after exposure to nitrobenzene. Benzene is not observed on the heavily oxidized surfaces.

INTRODUCTION

Molecules containing nitrogen atoms are notorious as poisons for many catalytic processes on transition metal surfaces, provided that the nitrogen atom is not fully saturated. Maxted (1) has shown that the poisoning is due to the bonding of the nitrogen atom to the surface. These molecules usually coordinate to metal cations in many metal compounds through the nitrogen lone pair electrons. By analogy with this, similar bonding schemes have been generally applied in the adsorption of nitrogen-containing molecules on transition metals. However, there are some doubts about the proposal that a nitrogen atom in a molecule prefers to associate with an adsorbent metal atom only by

this type of bonding since the molecule is classified as a rather hard base and the metal as a soft acid or base depending on particular cases (2).

To get some insight into the problem, the adsorption of benzene, pyridine, aniline, and nitrobenzene on evaporated nickel and iron has been studied by X-ray photoelectron spectroscopy. Recent uv photoelectron spectroscopic studies have shown that benzene remains intact on a nickel surface and does not significantly rehybridize upon chemisorption but instead forms a π-chemisorbed species (3). The adsorbed state of benzene will be very informative in discussing the other adsorption systems studied. Pyridine, aniline, and nitrobenzene are representative molecules which have a nitrogen in an aromatic
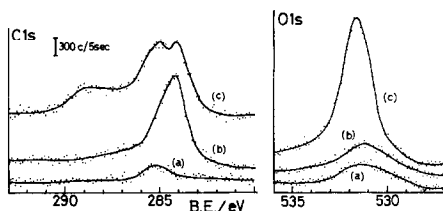
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FIG. 1. C 1s and O 1s spectral regions at 300°K for (a) nickel film, (b) after exposure to 10 L benzene, (c) subsequently to 15 L of acetic acid.

ring, in an amine group, and in a nitro group, respectively.

The effect of the presence of surface oxide or oxygen on the adsorption bonds of these molecules have also been studied by admitting these molecules to oxygen-pretreated nickel and iron surfaces. In studying the adsorbed states of large molecules by X-ray photoelectron spectroscopy, the data on core electron binding energies are not always sufficient for the characterization and identification of the adsorbed species. In such cases the spectral changes after some chemical perturbations of the adsorbed species can be very helpful in the characterization. Acetic acid, which can adsorb as acetate to the same extent both on evaporated and on preoxidized nickel and iron (4), has been employed for this purpose.

METHODS

Spectroscopic data were obtained using an AEI ES200 electron spectrometer with modified sample probe, metal evaporation, and baking arrangements. The nickel and iron films were prepared by evaporation from an electrically heated hairpin-shaped filament (0.6 mm in diameter, $>99\%$ purity) onto the sample probe whose temperature was maintained at about 295°K during evaporation. The pressure was less than 1×10^{-6} Pa after evaporation had ceased, but then usually fell to the base pressure, $<2 \times 10^{-8}$ Pa. When measuring the spectra (AlK_α as X-ray source), the pressure increased to 5×10^{-8} Pa because

of the poorer vacuum in the analyzer chamber. All binding energies, relative to the Fermi level, were determined by using the Ni $2p_{\frac{3}{2}}$ value of 852.9 eV or the Fe $2p_{\frac{3}{2}}$ value of 706.8 eV (5) of metallic nickel or iron as reference.

Benzene, pyridine, aniline, nitrobenzene, and acetic acid were obtained from Nakarai Chemicals and degassed by a series of freeze-pump-thaw cycles. Oxygen gas from Takachiho Kagaku Kogyo was passed through a liquid nitrogen trap before use. The gaseous molecules were admitted into the reaction chamber in the pressure range 10^{-6}–10^{-4} Pa.

Photoelectron peak intensities will be discussed on the basis of peak areas for C 1s, N 1s, and O 1s core electrons and of peak heights for Ni $2p_{\frac{3}{2}}$ and Fe $2p_{\frac{3}{2}}$ electrons because of the large asymmetry of their peaks. The thickness of surface oxide or adsorbates, d, has been estimated roughly using Eq. (1). The intensity of the Ni $2p_{\frac{3}{2}}$ or

$$I'/I = \exp(-d/\lambda \cdot \sin \theta) \qquad (1)$$

Fe $2p_{\frac{3}{2}}$ peak from metallic nickel or iron, I, decreases to I' when the core electrons escape into the vacuum through the surface oxide or adsorbates; θ is the angle of collection (with respect to the sample plane; 60° in the present experiment) of the photoelectrons; λ is the escape depth of the electrons in the surface layers and assumed to be 1.3 and 1.4 nm for Ni $2p_{\frac{3}{2}}$ and Fe $2p_{\frac{3}{2}}$ electrons, respectively (6). When d is smaller than the value for a monolayer, it is used to estimate the surface coverage.

RESULTS

Benzene

Figure 1 shows C 1s and O 1s spectra for the as-prepared nickel film and after exposure to benzene at 300°K. After a benzene exposure of 10 L (1 L = 1.3 $\times 10^{-4}$ Pa·sec), a C 1s peak (full width

at half maximum height = 1.7 eV) de-
velops centered at 284.2 eV. The intensity
of the Ni 2p$_4$ peak decreases by 10%.
A weak contaminant O 1s peak was ob-
served. After a subsequent 15-L exposure
to acetic acid, other C 1s peaks appear at
288.9 and 285.3 eV and O 1s at 531.6 eV
with diminution of the C 1s intensity at
284.2 eV by ~20%.

Exposure of evaporated nickel to O$_2$
(2 L) gives an O 1s peak at 529.9 eV and
decreases the intensity of Ni 2p$_4$ from
metallic nickel by 6%. The surface was
then exposed to benzene (20 L). The
resulting C 1s intensity at 284.2 eV is
one-half of that for the unoxidized nickel
surface.

When the evaporated nickel is exposed
to O$_2$ (150 L), the Ni 2p$_4$ peak diminishes
in intensity by 50%. No adsorbed species
is detected on the preoxidized surface after
30 L benzene exposure.

After evaporated iron is exposed to ben-
zene (30 L), a C 1s peak emerges at
284.5 eV (fwhm = 1.7 eV) and the inten-
sity of the Fe 2p$_4$ peak decreases by 11%.
The C 1s at 284.5 eV shows a tail on the
low binding energy side of the peak when
compared with the profile of the C 1s peak
due to the adsorbed benzene on nickel.

Pyridine

Exposure of nickel to pyridine (5 L) at
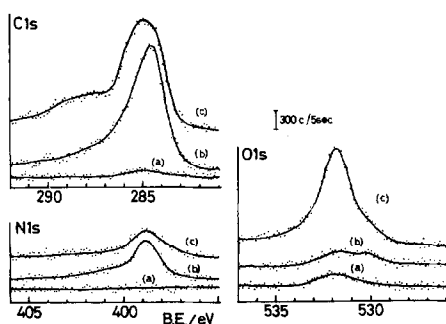300°K results in the emergence of a C 1s

FIG. 2. C 1s, N 1s, and O 1s spectral regions at
300°K for (a) nickel film, (b) after exposure to 5 L
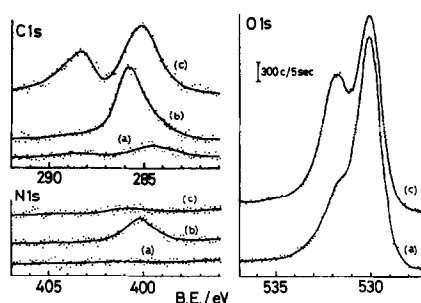pyridine, (c) subsequently to 6 L of acetic acid.

FIG. 3. C 1s, N 1s, and O 1s spectral regions at
300°K after exposure of nickel film to (a) 100 L
of O$_2$, (b) 5 L of pyridine, (c) 1 L of acetic acid,
in succession.

peak at 284.5 eV (fwhm = 2.0 eV) and
an N 1s at 398.8 eV (1.7 eV) as shown in
Fig. 2, and a diminution of the Ni 2p$_4$
peak intensity by 12%. Both the N 1s
and C 1s peaks show distinct tails on the
high binding energy side. The C 1s/N 1s
intensity ratio (peak area) is about 3.5
(without correction for different analyzing
energies). Subsequent exposure of the ad-
layer to acetic acid (6 L) decreases the
N 1s intensity by ~25% and gives weak
C 1s peaks around 288.6 and 285 eV and
an O 1s peak at 531.8 eV.

When the evaporated nickel is exposed
to O$_2$ (2 L) and then to pyridine (1 L),
C 1s and N 1s peaks appear at 285.4 eV
(fwhm = 2.8 eV) and at 399.9 eV (2.4 eV),
respectively, with shoulders on the low
binding energy sides of the peaks. No
change in the intensities of these peaks is
observed after a further 15-L pyridine ex-
posure. The C 1s/N 1s intensity ratio is
about 3.6.

Figure 3 shows C 1s and N 1s spectra ob-
tained after exposing a nickel surface to O$_2$
(100 L) and to pyridine (5 L), in succes-
sion. Single C 1s and N 1s peaks are ob-
served at 285.7 eV (fwhm = 1.8 eV) and
at 400.1 eV (1.8 eV). The pyridine ad-
sorption is followed by a decrease in the
intensities of the O 1s peak at 530 eV by
8% and the Ni 2p$_4$ peak by 13%. The C 1s
and N 1s peaks are easily removed by
subsequent exposure to acetic acid (only

1 L), followed by the appearance of C 1s peaks at 285.1 and 288.4 eV and an O 1s peak at 531.9 eV.

Exposure of iron to pyridine (10 L) results in the appearance of broad C 1s peaks at 284.4 eV (fwhm = 2.5 eV) and N 1s peaks at 398.9 eV (3.2 eV) and the diminution of the Fe 2p$_3$ intensity by 15%. The C 1s/N 1s intensity ratio is about 3.4. After heating the adlayer at 320°K for 10 min, the N 1s at 398.9 eV loses half of its intensity with a shift of the N 1s peak maximum to 397.6 eV. A shoulder around 283.7 eV appears with the C 1s at 284.4 eV.

When evaporated iron is exposed to O$_2$ (2 L) and to pyridine (10 L), in succession, the C 1s and N 1s peaks appear at 285.7 eV (fwhm = 2.4 eV) and at 400.0 eV (1.9 eV), respectively. The intensities of the Fe 2p$_3$ peak and the O 1s peak at 530 eV decrease by 10 and 3%, respectively, during the pyridine adsorption. Pyridine adsorbed on iron heavily oxidized by O$_2$ (100 L) shows a C 1s at 285.9 eV (2.4 eV) and an N 1s at 400.2 eV (1.9 eV) associated with decrease in intensities of the Fe 2p$_3$ and the O 1s at 530 eV by 7 and 4%, respectively.

Aniline

Exposure of nickel surface to aniline (10 L) at 290°K results in a C 1s peak at 284.6 eV (fwhm = 2.3 eV) and N 1s at 398.1 (~1.6 eV) and 400.2 eV (~1.5 eV), as shown in Fig. 4, and a diminution of the Ni 2p$_3$ peak intensity by 13%. The intensity ratio of the two N 1s peaks is quite sensitive to a small change of the sample temperature. After heating the adlayer at 320°K for 10 min, the N 1s peak at 400.2 eV loses one-third of its intensity but the peak at 398.1 eV gains the same amount in intensity. A separate experiment showed that the N 1s at 400.2 eV disappeared almost completely at 370°K while that at 398.1 eV increased in intensity. The N 1s at 400.2 eV, obtained after exposure of evaporated nickel to aniline (10 L), decreased in intensity only by 20%

on subsequent exposure to acetic acid (150 L) while that at 398.1 eV showed no change.

When nickel surface is exposed to O$_2$ (300 L), the Ni 2p$_3$ intensity diminished by 54%. The surface is then exposed to aniline (2 L). An N 1s peak develops at 400.1 eV (fwhm = 1.8 eV) associated with a weak peak at 398 eV and with a C 1s at 285.1 eV (2.0 eV). During the aniline adsorption, the Ni 2p$_3$ peak from metallic nickel diminishes in intensity by 17% and the O 1s at 530 eV by 13%. The N 1s intensity at 400.1 eV decreases by 70% on heating the adlayer at 370°K for 10 min with no change in intensity of the N 1s at 398 eV or by 60% on exposure of the adlayer to acetic acid (10 L).

When iron is exposed to aniline (10 L) at 290°K, N 1s peaks are observed at 400.0 and 398.0 eV (with a tail on the low binding energy side) as shown by Fig. 5a and a C 1s at 284.7 eV. The N 1s intensity at 398.0 eV is stronger than that at 400.0 eV. The Fe 2p$_3$ intensity diminishes by 20%. On heating the adlayer at 320°K for 20 min, the N 1s at 400.0 eV disappears and the peak at 398.0 eV shifts
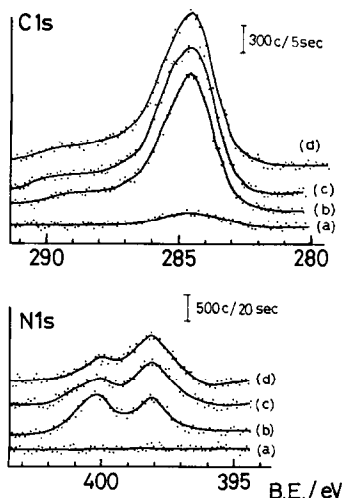

FIG. 4. C 1s and N 1s spectral regions for (a) nickel film, (b) after exposure to 10 L of aniline at 290°K, (c) after heating (b) at, 320°K for 10 min, (d) further heating at 320°K for 10 min.

to 397.5 eV with no change in intensity. A separate experiment showed that the N 1s at 400.0 eV was readily removed by subsequent exposure to acetic acid (10 L) but the peak at 398.0 eV showed no change in intensity.

Figure 5 shows the effect of preoxidation of the iron surface on aniline adsorption. The diminution of the Fe $2p_i$ peak from metallic iron is 11 and 58%, respectively, after 2 L and 100 L exposure to O_2. In the latter case, the Fe $2p_i$ peak from the oxide is clearly shown with a shift of ~3.5 eV from that for metallic iron. With increasing extent of oxidation the N 1s at 398.0 eV shows a smaller intensity. The N 1s at 400.2 eV is predominant on the preoxidized surfaces. With iron preoxidized by 2 L exposure to O_2, the O 1s at 530 eV decreases in intensity by 25% after subsequent 100 L aniline exposure and about the same intensity for the O 1s peak emerged at 531.8 eV. The diminution of the Fe $2p_i$ intensity is about 20%. The N 1s peak at 400.0 eV, in the case of Fig. 5c, decreases in intensity to one-fifth by heating the adlayer at 370°K for 10 min with no change in intensity at 398 eV and disappears quickly by subsequent 3 L exposure to acetic acid.

Nitrobenzene

Figures 6 and 7 show N 1s, C 1s, and O 1s spectra obtained after exposing an
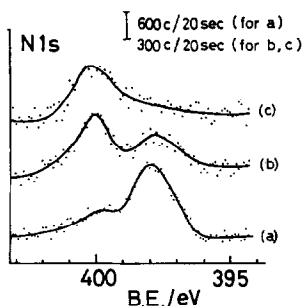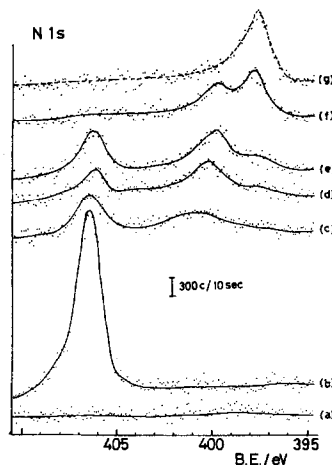
FIG. 6. N 1s spectral region for the nitrobenzene/nickel film adsorption system. (a) Cooled to 90°K, (b) after 7 L exposure at 90°K, (c) warmed to 140°K, (d) to 170°K, (e) after 10 L exposure at 170°K, (f) warmed to 295°K, (g) 10 L exposure entirely at 295°K.

evaporated nickel surface at 90°K to nitrobenzene, followed by warming to 295°K. The surface was contaminated to some extent during cooling to 90°K as shown by the increase in the C 1s and O 1s peak intensities. Exposure of nitrobenzene (7 L) at 90°K results in an N 1s peak at 406.5 eV, a C 1s at 285.3 eV, and an O 1s at 533.3 eV. On warming to 140°K the N 1s at 406.5 eV and the O 1s at 533.3 eV lose much intensity. Another N 1s peak appears at 400.7 eV and associated with this is a distinct O 1s shoulder at 531 eV. On further warming to 170°K, the N 1s at 400.2 eV

FIG. 5. N 1s spectral region after exposure to 10 L of aniline at 290°K for (a) clean iron, and iron films pretreated by O_2, (b) 2 L, (c) 100 L.
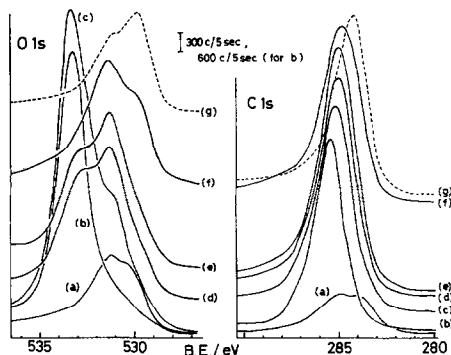
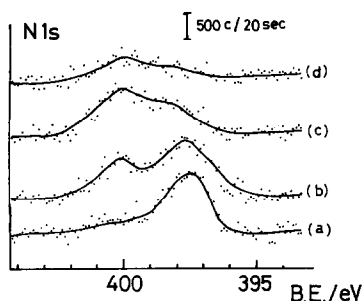FIG. 7. C 1s and O 1s spectral regions as for Fig. 6.

FIG. 8. N 1s spectral region after exposure to 10 L of nitrobenzene at 295°K for (a) clean iron, and iron films pretreated by O_2, (b) 2L, (c) 100 L, (d) 300 L.

and the O 1s at 531.3 eV are intensified, followed by the appearance of a weak N 1s peak at 398 eV. The C 1s peak maximum shifts to 284.9 eV. At this temperature, the adlayer is again exposed to nitrobenzene (10 L). The peaks at 399.8 and 406.3 eV increase slightly. On warming the adlayer finally to 295°K, the N 1s at 406 eV disappears completely and the peak at 397.7 eV gains much in intensity at the expense of the one at 399.7 eV. The O 1s at 533.3 eV disappears and the one at 531.5 eV decreases in intensity giving a distinct peak at 530 eV.

Exposure of a nickel surface to nitrobenzene (10 L) entirely at 295°K results in an N 1s peak at 397.6 eV (fwhm = 1.7 eV) with a weak tail on the high binding energy side, an O 1s at 529.9 eV with a shoulder around 531.5 eV, and a C 1s at 284.2 eV (2.0 eV) as shown by Figs. 6 and 7g. The diminution of the Ni 2p₃ intensity is 28%. The O 1s/N 1s intensity ratio is 2.4 and the C 1s/N 1s ratio is 4.4.

Exposure of a nickel surface to O_2 (150 L) leads to a decrease in intensity of the Ni 2p₃ peak by 49%. After a subsequent 10 L nitrobenzene exposure a weak N 1s peak develops at 400 eV with a shoulder around 398 eV. Associated with the N 1s are the O 1s at 531.5 eV (as a shoulder of the strong peak at 529.9 eV) and the C 1s at 284.8 eV. On heating the adlayer at 370°K for 10 min, the N 1s

peak at 400.0 eV decreases in intensity to show no clear maximum and the one around 398 eV is intensified to give a distinct peak maximum at 398.6 eV (fwhm = 2.7 eV).

Iron surface exposed to nitrobenzene gives an N 1s peak at 399.9 eV even at 90°K together with one at 406.4 eV. During warming to 295°K the N 1s at 399.9 eV decreases in intensity, followed by the appearance of a peak at 397.6 eV. Exposure of iron to nitrobenzene (10 L) entirely at 295°K gives C 1s, N 1s, and O 1s at 284.6, 397.6, and 529.9 eV (with a shoulder around 531.2 eV), respectively, and a diminution of the Fe 2p₃ peak intensity by 24%. The N 1s peak at 397.6 eV shows no change after a subsequent 10 L acetic acid exposure.

Figure 8 demonstrates the effect of oxygen treatment on the nitrobenzene adsorption. With increasing the oxygen exposure to 100 L, the N 1s peaks increase in intensity at 400.0 eV but decrease at 397.7 eV. The C 1s peak is observed around 284.6 eV. On heating at 370°K for 10 min, the N 1s at 400.0 eV disappears almost completely but the peak at 397.7 eV shows no change. When iron is exposed to O_2 (300 L), the Fe 2p₃ peak due to oxidized iron (3.7 eV lower in binding energy than metallic iron) is stronger than that for the metal. On the surface the N 1s around 398 eV is very weak and the peak at 400.0 eV is also considerably weaker than that obtained for the surface exposed to O_2 (100 L).

DISCUSSION

Benzene

uv photoelectron spectroscopy shows that benzene is chemisorbed on nickel through the π-electrons of the ring (3). The C 1s binding energy, 284.2 eV, of adsorbed benzene on nickel is lower by 0.8 eV than that of condensed benzene on gold, 285.0 eV. A carbide-like species also

gives low binding energy of C 1s around 283 eV (7, 8) but the measured C 1s spectrum shows no peak around 283 eV. The C 1s at 284.2 eV is reasonably assigned to molecularly π-bonded benzene.

Benzene adsorbed on iron (C 1s = 284.5 eV) also seems to be chemisorbed by π-d electron interaction. The weak tail on the low binding energy side (around 283.5 eV) of the C 1s peak may suggest that some benzene loses a proton on adsorption, forming, for example, a phenyl species as suggested by Anderson and Kemball (9), because a direct carbon–metal σ bond is expected to show a C 1s value close to that for a carbide-like species. As discussed later, a direct nitrogen–metal bond in adsorbed nitrobenzene also shows N 1s (397.7 eV) close to that for a nitride-like species (397 eV) (10–12).

From the attenuation of the Ni 2p$_\frac{3}{2}$ and the Fe 2p$_\frac{3}{2}$ intensities, 10 and 11%, during benzene adsorption, the thickness of the adsorbate can be estimated using Eq. (1) to be about 0.12 and 0.14 nm, respectively. The π-chemisorbed benzene on nickel is not readily displaced by acetic acid.

The attenuation of the Ni 2p$_\frac{3}{2}$ intensity, 6%, after 2 L O$_2$ exposure gives an estimate of $\sim$0.07 nm for the surface oxide thickness, suggesting that less than half of the surface is covered with oxygen. The amount of benzene adsorbed on the surface is estimated to be about half that on clean nickel from the C 1s intensities and the attenuation of the Ni 2p$_\frac{3}{2}$ intensities. The C 1s binding energy does not shift in the presence of oxygen on the surface. Benzene seems to locate itself on unoxidized nickel atoms. Nickel exposed to 150 L O$_2$ gives a surface oxide, estimated to be about 0.8 nm thick, and does not chemisorb benzene. This is in sharp contrast to the adsorption of pyridine and aniline.

Pyridine

Pyridine has been suggested to adsorb on nickel perpendicularly to the surface through the nitrogen atom using lone pair electrons; this derives from the data of exclusive H/D exchange at the 2 and 6 positions in the ring on nickel catalysts (13). We reported pyridine adsorbed perpendicularly to the surface of evaporated nickel and iron under poorer vacuum conditions ($\sim$10^{-4} Pa) following a study of uv absorption spectra (14). Sheets and Hansen (15) have reported an adsorption of pyridine on nickel promoted by oxygen and CO pretreatment.

The C 1s and N 1s peaks of pyridine adsorbed on heavily oxidized (by 100 L O$_2$) metals (285.7 and 400.2 eV for nickel and 285.9 and 400.2 eV for iron) locate at almost the same binding energies as those for condensed pyridine, 286.0 and 400.0 eV. Pyridine adsorbed on the Lewis acid centers of metal oxides also shows peaks with these binding energies, while pyridine on Brønsted acid sites gives peaks at 286 and 402 eV (16). The former species is assigned to the pyridine bonding to the metal ion through nitrogen lone pair electrons and the latter to the pyridinium ion. Therefore, pyridine adsorbed on preoxidized nickel and iron is attributed to the molecule bonding to the surface oxide through nitrogen. The adsorbed species are quite readily expelled by acetate on exposing the adlayer to acetic acid as shown by the disappearance of the N 1s peak at 400 eV and the C 1s at 286 eV.

Pyridine adsorbed on evaporated nickel and iron shows C 1s and N 1s (284.5 and 398.8 eV for nickel; 284.4 and 398.9 eV for iron) which are about 1.3 eV lower in binding energy than those on the preoxidized surfaces but much higher than those for carbide- or nitride-like species (283 eV (7, 8) and 397 eV (10–12), respectively). The latter fact suggests that the adsorbed pyridine remains in the molecular form. The C 1s/N 1s intensity ratio of condensed pyridine, 3.3, is retained on adsorption: 3.5 for nickel, 3.4 for iron, and 3.6 for preoxidized nickel. Pyridine ad-

sorbed on the evaporated metals is not readily removed by subsequent exposure to acetic acid like benzene adsorbed on the metals, although acetic acid can produce about the same amount of acetate on evaporated and preoxidized nickel and iron (4). Pyridine adsorbed on the evaporated metals differs from that on preoxidized metals in the interaction to acetic acid and binding energies of C 1s and N 1s peaks as discussed above and, consequently, in the chemical bonding character to the surfaces. The shifts of the C 1s and the N 1s to lower binding energy imply an increase in electron density on the pyridine ring and/or a larger relaxation energy on adsorption. This is expected when pyridine chemisorbs on nickel and iron with π-d interaction as is found in the benzene-nickel system. The diminution of the Ni 2p$_\frac{3}{2}$ and the Fe 2p$_\frac{3}{2}$ intensities, 12 and 15%, on pyridine adsorption is a little larger than those observed on benzene adsorption, indicating, together with the stronger C 1s intensity of the pyridine, that the amount of adsorbed pyridine is larger on nickel and iron than that of the adsorbed benzene, i.e., there is stronger adsorption of pyridine than benzene. This may correspond to the larger shifts of C 1s and N 1s on pyridine adsorption and may be due to the difference in the energy of the π^* level between the two molecules.

The large fwhm values for the C 1s and the N 1s peaks of the pyridine adsorbed on iron suggest the presence of different adsorbed states. On heating the adlayer at 320°K, the N 1s at 398.9 eV lost much intensity but the peak at 397.6 eV gained in intensity, associated with a weak C 1s at 283.7 eV. The N 1s binding energy, 397.6 eV, is the same as that for the C₆H₅N(ads) anion from aniline and nitrobenzene, as discussed later, suggesting a direct nitrogen–metal bonding. The C 1s at 283.7 eV is quite low in energy and close to the low binding energy of C 1s observed on benzene adsorption on iron, suggesting

the formation of a direct carbon–iron bond. Therefore, the C 1s and N 1s peaks may arise from the pyridine bonding to iron through both the nitrogen atom and the carbon atom at the 6-position which released the proton, the molecules lying with their rings at some large angle to the surface as suggested for high temperature adsorption of pyridine on platinum (17). The species at elevated temperature is likely to explain the exclusive H/D exchange at the 2- and 6-positions in the pyridine ring on nickel catalysts (13).

Approximately 30% of the surfaces are covered by oxygen on nickel and iron after 2 L O₂ exposure. The predominant adsorbed state of pyridine on the surfaces is the one bonding through nitrogen revealed by the N 1s peak at 400 eV. A small amount of π-bonded species also exists as shown by the distinct tail on the low binding energy side of the 400 eV peak.

Our previous uv absorption results for pyridine adsorption (14) presumably correspond to the pyridine on an oxygen-covered surface owing to the poorer vacuum used.

Aniline

Oxidation of nickel and iron surfaces by O₂ (300 and 100 L, respectively) gives a surface oxide estimated to be about 0.8 to 0.9 nm thick from the diminution of the Ni 2p$_\frac{3}{2}$ and the Fe 2p$_\frac{3}{2}$ intensities. The C 1s and the N 1s peaks, 285.1 and 400.1 eV for nickel and 285.0 and 400.2 eV for iron, due to adsorbed aniline on the surfaces locate at virtually the same binding energies as those for condensed aniline on gold, 285.1 and 399.9 eV. These species desorb considerably on exposure to acetic acid or by heating the adlayer at 370°K. These results are quite similar to those with pyridine on the oxidized metals. Ethylenediamine (1,2-diaminoethane), a typical chelating agent, adsorbed on the preoxidized nickel and iron also shows C 1s and N 1s peaks whose binding energies are

the same as those for the condensed system (4). Therefore, it is concluded that aniline adsorbed on the preoxidized surfaces bonds through nitrogen lone pair electrons. In addition to the above conclusion, the diminution of the metal peak intensities are found to be a little larger than that of the O 1s peak at 530 eV in all three kinds of molecule when adsorbed on the preoxidized nickel and iron through nitrogen lone pair electrons. This is probably due to the fact that the kinetic energy of the O 1s electron is larger than that of Ni $2p_{\frac{1}{2}}$ and Fe $2p_{\frac{1}{2}}$ electrons and some of the oxygen atoms are present in the same layer with the adsorbates while all metallic nickel and iron atoms are underneath the layer of the adsorbates. On the preoxidized nickel surface aniline is more stable to displacement by acetic acid than pyridine. The N 1s peak at 398 eV is very weak on the oxidized surfaces but is observed as a stronger peak on evaporated metals.

Adsorption of aniline at 290°K gives a C 1s peak at 284.6 eV and two N 1s peaks at 400.2 and 398.1 eV (with about the same intensity) on the evaporated nickel surface and a C 1s at 284.7 eV and two N 1s at 400.0 eV (weak) and at 398.0 eV (strong) on the iron surface. This implies the presence of two kinds of adsorbed species on the surfaces, together with a different behavior of the two N 1s peaks after exposure to acetic acid and heating.

The N 1s peak at 398.0 eV (on iron) is 1.9 eV lower than that for condensed aniline. The shift is much larger than that with C 1s, 0.5 eV, unlike the case of pyridine. The large N 1s shift, therefore, indicates the formation of much more negative nitrogen, namely an anionic species. The binding energy, however, is not as low as that for nitride-like species, 397 eV. Adsorption of hydrazine on iron at 295°K (18) leads to dissociation giving nitrogen adatoms (N 1s at 397 eV) and, after further exposure, to more adsorbed species. NH (ads) (N 1s at 398 eV) and

N$_2$H$_4$ (ads) (N 1s at 400 eV). Exposure of nickel and iron to ethylenediamine results in the appearance of two N 1s peaks, 400.0 and 397.7 eV, at 290°K with virtually the same intensity (4). From these data, the amine group of aniline is considered to release a proton. Adsorption of aniline on iron oxidized by O$_2$ (2 L) decreases the O 1s peak at 530 eV due to surface oxygen by 25% and gives the same amount of O 1s at 531.8 eV. The diminution of the O 1s peak at 530 eV is larger than that of the Fe $2p_{\frac{1}{2}}$, suggesting a different type of adsorption from the one merely through nitrogen lone pair electrons where the diminution of O 1s at 530 eV is a little smaller than that of the metal peaks. These facts are explained by the formation of –O–H groups (giving O 1s at 531.8 eV) in the reduction of surface oxygen (530 eV) with hydrogen released from a part of the amine group of aniline and are consistent with the dissociation of the amine group as concluded by the N 1s binding energy. Ethylenediamine can also reduce the surface oxygen on nickel giving water if the oxygen coverage is less than one monolayer (4). Heating the adlayer on iron to 370°K shifts the N 1s peak from 398.0 to 397.6 eV. The latter binding energy is the same as that for C$_6$H$_5$N (ads) from nitrobenzene to be discussed below. The most probable species giving N 1s at 398.0 eV is, therefore, an anionic C$_6$H$_5$NH (ads) or C$_6$H$_5$N (ads). The former species is more probable if the shift to 397.6 eV arises from further dissociation of the C$_6$H$_5$NH (ads) to C$_6$H$_5$N (ads). The species is not displaced by acetate after exposure to acetic acid. On evaporated iron, the N 1s peak at 398.0 eV is predominant even at 290°K. The amine group of aniline is less reactive to the nickel than to the iron.

However, the dissociation of aniline into a phenyl group and NH$^-$ is not excluded at present because hydrogenation of aniline over nickel leads, besides cyclohexylamine, to side-reaction products such as diphenyl-

amine, phenylcyclohexylamine, cyclohexane, benzene, and ammonia (19).

The N 1s peak at 400.2 eV on nickel is very close to those for the aniline on the preoxidized metals and condensed aniline. However, the C 1s shows a 0.5 eV shift and the N 1s is not readily removed by acetic acid unlike the case with the preoxidized metals, suggesting that the N 1s and the C 1s may be due to species which bond with nickel rather by π-electrons of the aromatic ring as with benzene. An N 1s shift is not expected for such species because the nitrogen atom is outside the ring. The spectral change on heating shows that such species change into the anionic species. On oxidized nickel and iron, aniline chemisorbed through nitrogen desorbs without changing into the anionic species during heating.

Nitrobenzene
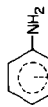
On warming nickel exposed to nitrobenzene at 90°K, the C 1s, N 1s, and O 1s peaks due to condensed nitrobenzene (285.7, 406.5, and 533.6 eV) decrease in intensity, resulting in the emergence of peaks at 400.7 and 531 eV at 140°K, which become predominant at 170°K associated with shifts to 400.2 and 531.3 eV, respectively. The clear C 1s is observed at 284.9 eV. On warming to 295°K, these peaks transfer into the ones which are predominant on the adsorption of nitrobenzene entirely at 295°K, namely, 284.2, 397.6, and 530.0 eV. The fairly large shifts of these binding energies from those for condensed nitrobenzene demonstrate unambiguously a dissociative chemisorption of nitrobenzene on nickel.

Adsorption of NO_2 on evaporated nickel films has been studied by Brundle (10). At 80°K NO_2 dissociates to NO with loss of O and then it begins to form a condensed layer. On warming to 300°K further dissociation of NO_2 and NO occurs to yield oxide and nitride (with some chemisorbed NO remaining). Adsorption of NO

on nickel (10, 11a, 12) also results in dissociative chemisorption with loss of oxygen which is retained at the surface. The majority of the nitrogen, however, is lost from the surface, more than 80% in the case of NO at room temperature (10, 12). The developments of the O 1s peak at 530 eV, characteristic of surface oxygen, and the N 1s at 397.6 eV, close to that for nitride-like species, mean the dissociation of the nitro group of nitrobenzene on nickel at 295°K producing negative charged nitrogen and chemisorbed oxygen. The O 1s (530 eV)/N 1s (397.6 eV) intensity ratio, 2.4, is quite consistent with the value, 2.6, for condensed nitrobenzene. This means no loss of nitrogen from the surface in the dissociation of nitrobenzene, unlike the cases of NO and NO_2 dissociation. This strongly suggests that the carbon–nitrogen bond rupture does not occur in the dissociative chemisorption because the loss of nitrogen should happen after the bond rupture. The C 1s (284.2 eV)/N 1s (397.6 eV) intensity ratio, 4.4, is close to the value for condensed nitrobenzene, 3.9. The small difference is probably due to hydrocarbon contamination occurring simultaneously with nitrobenzene adsorption.

The spontaneous dissociation of the nitro group at 295°K is quite consistent with hydrogenation reaction data of nitrobenzene. Nitro groups attached to aromatic rings are readily reduced by hydrogen on nickel catalysts at moderate temperatures and pressures and the molecules are, in general, cleanly reduced to the corresponding amines in very high yield (20). The high yield implies no or very little percentage of cleavage of the aromatic ring or the rupture of the carbon–nitrogen bond, in good consistency with the conclusion discussed above. From these results, nitrobenzene is considered to form an anionic species, C_6H_5N(ads). The magnitude of the negative charge of the species is not clear but the charge on the nitrogen is assumed to be close to that for nitrogen

TABLE 1

Proposed Adsorbed States of Benzene, Pyridine, Aniline, Nitrobenzene on Evaporated and Preoxidized Nickel and Iron, and Their Core Electron Binding Energies (in eV)

	Condensed	Adsorbed on evaporated		Adsorbed on preoxidized	
		Nickel	Iron	Nickel (~0.8 nm thick oxide)	Iron (~1 nm)
	C 1s N 1s O 1s	C 1s N 1s O 1s (exposure; attenuation of metal peak)	C 1s N 1s O 1s	C 1s N 1s O 1s (exposure; attenuation of metal and O 1s)	C 1s N 1s O 1s
Benzene	285.0	(10 L; 10%) 284.2	(30 L; 11%) 284.5	(30 L) No adsorption	
Pyridine	286.2, 400.1	(5 L; 12%) 284.5, 398.8	(10 L; 15%) 284.4, 398.9	(5 L; 13%, 8%) 285.7, 400.1	(10 L; 7%, 4%) 285.9, 400.2
Aniline	285.1, 399.9	(10 L; 13%) 284.6, 400.2 / 284.6, 398.1	(10 L; 20%) 284.7, 400.0 / 284.7, 398.0	(2 L; 17%, 13%) 285.1, 400.1	(10 L; 11%, 8%) 285.0, 400.2
Nitrobenzene	285.3, 406.5, 533.3	284.9, 400.2, 531.3 (10 L; 28%) / 284.2, 397.6, (530.0 "O")	Predominant at low temperature / 285, 399.9, 531 (10 L; 24%) Predominant at room temperature / 284.6, 397.6, (529.9 "O")	(10 L) / 284.8, 400.0 / 284.8, 398 (530.0 "O")	Predominant / 284.6, 400.0 / 284.6, 397.7, (530 "O")

adatoms on nickel and iron. The C 1s at 284.2 eV is 1.5 eV lower than that for condensed nitrobenzene, being not inconsistent with the formation of the anionic species. Nitrobenzene also gives the same anionic species on iron.

The diminution of the Ni 2p$_{\frac{3}{2}}$ intensity by 28% after exposure to nitrobenzene at 295°K is much larger than those observed after exposure to benzene (10%), pyridine (12%), and aniline (13%). The thickness of the overlayer is estimated to be about 0.4 to 0.5 nm. This implies adsorption of the anionic C$_6$H$_5$N(ads) on top of the very thin oxide layer formed by the dissociation of the nitro group.

The C 1s at 284.9 eV, N 1s at 400.2 eV, and O 1s at 531.3 eV being predominant at 170°K can be assigned to an intermediate between nitrobenzene and the C$_6$H$_5$N(ads). The N 1s and O 1s binding energies are much smaller, by 6.3 and 2.3 eV, respectively, than those for condensed nitrobenzene and rather close to those for nitrosobenzene in the solid state, 401.6 and 532.6 eV (21). The intermediate is, therefore, ascribable to adsorbed nitrosobenzene, C$_6$H$_5$NO(ads), being analogous to the formation of NO(ads) on the adsorption of NO$_2$. Some electron accumulation on the NO group is expected on the adsorption, from the binding energy difference, about 1.3 eV, between solid and adsorbed nitrosobenzene. After warming to 295°K, the O 1s at 531.5 eV is stronger than that at 529.9 eV while the N 1s at 399.7 eV is smaller than that at 397.7 eV. This inconsistency in intensity is presumably explained by the overlap of the O 1s peak at 531 eV with that from −O−H species on the surface which might be produced by ambient gases during cooling. On nickel NO$_2$ can dissociate even at 80°K but nitrobenzene commences to dissociate at 140°K. On iron C$_6$H$_5$NO(ads) is produced even at 90°K.

The adsorption of nitrobenzene on nickel and iron at 295°K is dissociative at the nitro group leaving oxygen on the surfaces and, therefore, is expected to be influenced by the presence of oxygen on the surfaces. On the preoxidized iron surface the ratio C$_6$H$_5$NO(ads)/C$_6$H$_5$N(ads) varies depending on the extent of oxidation, as shown in Fig. 8. The surface oxide controls the dissociation of nitrobenzene at the stage of nitrosobenzene. The amount of C$_6$H$_5$NO(ads) is much larger on iron oxidized by 100 L O$_2$ than by 300 L O$_2$, indicating the importance of oxygen-deficient sites on the oxide for the formation of the C$_6$H$_5$NO(ads). The same conclusion is derived for the preoxidized nickel. Disappearance of the C$_6$H$_5$NO(ads) on the preoxidized iron after heating at 370°K reveals the desorption of nitrosobenzene from the surface oxide. On the preoxidized nickel, a part of the C$_6$H$_5$NO(ads) is found to change at 370°K into C$_6$H$_5$N(ads) as shown by the intensity increase at 398 eV.

CONCLUSION

In Table 1 are listed the proposed adsorbed states of benzene, pyridine, aniline, and nitrobenzene on the evaporated and the preoxidized nickel and iron, along with their core electron binding energies and those for condensed molecules. As discussed above, pyridine and aniline can adsorb through nitrogen lone pair electrons on oxygen-pretreated nickel and iron, as in metal coordination compounds. However, the pyridine and, partly, aniline seem to bond to clean nickel and iron surfaces rather by π-electrons as with benzene. Aniline and nitrobenzene form strongly chemisorbed anions on the metals, produced through the dissociation of the amine and nitro groups, respectively.

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