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X-Ray Photoelectron Spectroscopic Study of the Reaction of Evaporated Iron, Nickel, and Palladium with Nitric Oxide

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The reaction of the evaporated iron, nickel, and palladium with NO was investigated by X-ray photoelectron spectroscopy. On both iron and nickel larger part of NO dissociates to give two or more N(1s) and O(1s) photoelectron peaks which are ascribable to the surface oxide, nitride, and NO species. The proportion of these species is estimated roughly from the intensity ratios of the N(1s) and O(1s) peaks at 15 NO: 65 O: 20 N (iron) and 7 NO: 65 O: 28 N (nickel) when the metals are exposed to 5 Torr of NO gasfor 1 s, and 35 NO: 55 O: 10 N (iron) and 10 NO: 75 O: 15 N (nickel) when exposed to 10 Torr of NO for 10 min. On palladium the N(1s) for chemisorbed NO is observed. The N(1s) binding energies of the surface NO are compared with the N(1s) binding energies and the infrared NO frequencies of the corresponding transition metal nitrosyls.

The NO molecule has one electron in an antibonding π orbital and, in transition metal nitrosyls, bonds to a metal atom at various electronic states.[1] Two limiting species are linearly coordinated NO^+ and angularly coordinated (bent) NO^-. Chemisorbed NO on transition metals is expected to take various bonding and electronic structures. An electronic structure of NO has a significant resemblance to and yet a difference from CO and O_2 whose chemisorption has been widely investigated.

Infrared studies of NO adsorption on transition metals have been reported by Terenin and Roev,[2] Dunken and Hobert,[3] and Blyholder and Allen.[4] Two or more bands of NO stretching were observed for chemisorbed NO. These bands have been assigned to structures described as ionic, covalent, or coordinative[2] and discussed on correlating their frequencies to the extent of π back-bonding to NO.[4] Sachtler[5] has reported that NO partially dissociates on nickel and both chemisorbed NO and oxygen exist on the surface.

In the present paper, X-ray photoelectron spectroscopy (ESCA) is applied to observe the reaction of evaporated iron, nickel, and palladium in order to characterize the surface species and to check an existence of surface nitride.

Experimental

Metals were evaporated onto a stainless steel plate at 10^{-6} Torr as described elsewhere.[6] The evaporated metal film was exposed to the gas to be studied at room temperature after about 10 s from evaporation. After evacuation of the gas for 5 min, photoelectron spectra of the surface species formed were recorded. During the spectral measurement, the vacuum was maintained at 10^{-7} Torr.

NO gas was obtained from Takachiho Kagaku Kogyo. Spectra were recorded in 0.1 eV steps on a KES-X2001 (Kokusai Electric Co.) electron spectrometer using Al$K\alpha$ (for nickel and palladium) and Mg$K\alpha$ (for iron) X-radiation. The binding energy reference is the Fermi level which is taken as the inflection point of the low-energy edge of the 4d band of palladium according to Baer *et al.*[7]

Results

When evaporated iron was exposed to NO at a pressure of 5 Torr for about 1 s, the broad N(1s) peaks were observed at the binding energies of 396.6 and 400.7 eV (Fig. 1-a). Both minimum and maximum counting rates (counts/5 s) are shown in parentheses in the figures. The O(1s) peaks were at 530.0 and around 533.0 eV (Fig. 2-a). The Fe($2p_{3/2}$) were at 707.0 and around 709.8 eV (Fig. 3-a). The chemical shift of the latter peak is about 2.8 eV from the former which is due to metallic iron.

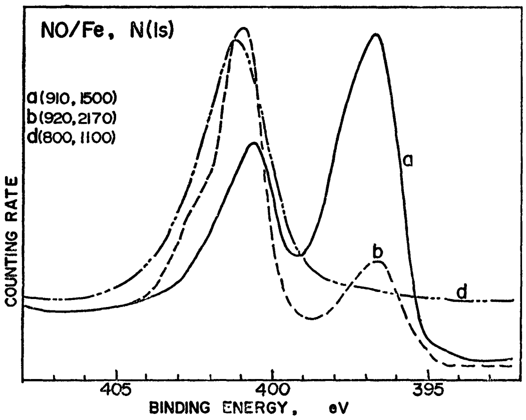

Fig. 1. N(1s) peaks from evaporated iron exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min, (d) 10 Torr of NO for 10 min after exposure to 20 Torr of air for 5 min.

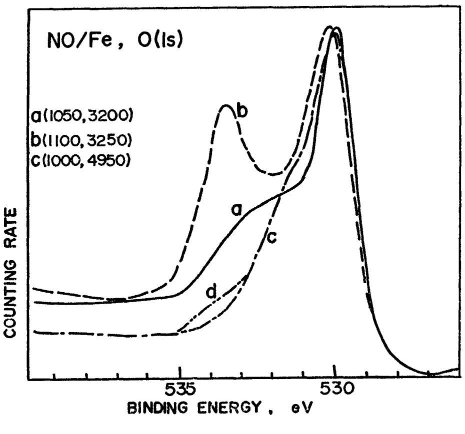

Fig. 2. O(1s) peaks from evaporated iron exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min, (c) 20 Torr of air for 5 min, (d) 10 Torr of NO for 10 min after c.

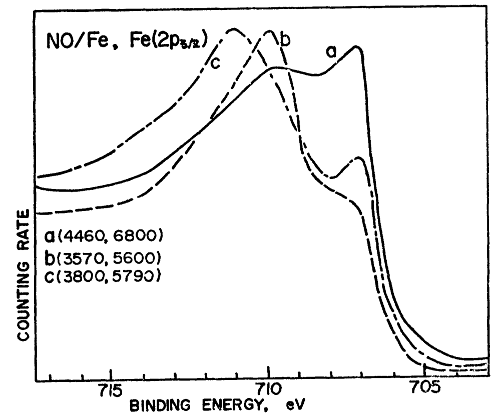

Fig. 3. Fe($2p_{3/2}$) peaks from evaporated iron exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min, (c) 20 Torr of air for 5 min.

Spectra b of Figs. 1 to 3 were recorded after evaporated iron was exposed to NO at a pressure of 10 Torr for 10 min. The N(1s) peaks are at 396.6 and 401.0 eV with a shoulder around 402.5 eV. The peak at 401.0 eV and the shoulder decreased in intensity with time during the spectral measurement while the 396.6 eV peak not at all. For example, the original 401.0 eV peak was depressed to one thirds after 1 hr. The N(1s), O(1s), and metal peaks (Figs. 1 to 3 for iron and 4 to 6 nickel) were recorded in this order within 1 hr. The 401.0 eV peak is considerably stronger in intensity than the 400.7 eV peak in Fig. 1-a. The O(1s) peaks are at 530.2 and 533.5 eV. The Fe($2p_{3/2}$) peaks are at 707.0 and 710.0 eV. The 707.0 eV peak due to metallic iron is further depressed from that of spectrum a.

Spectra c of Figs. 2 and 3 were recorded after evaporated iron was exposed to air at a pressure of 20 Torr for 5 min. The intense O(1s) peak was observed at 530.0 eV with a shoulder around 531.7 eV. The Fe($2p_{3/2}$) of oxidized iron shows a chemical shift of 4.0 eV from metallic iron which is 1.0 eV larger than when iron was exposed to NO. This surface oxide was subsequently exposed to NO at a pressure of 10 Torr for 10 min and spectra of Figs. 1 and 2 were recorded. The N(1s) electrons give only one broad peak at 401.3 eV and a weak O(1s) peak appeared at 533.7 eV. The above spectral data of N(1s) peaks are summarized in Table 1 with infrared data. The corresponding data of various compounds are also listed.

Spectra a of Figs. 4 to 6 were recorded after evaporated nickel was exposed to NO at a pressure of 5 Torr for about 1s. The N(1s) peaks are at 397.6 and around 400.2 eV. The O(1s) peaks are at 530.1, 531.7, and 533.3 eV. The Ni($2p_{3/2}$) spectrum shows a peak at 853.5 eV due to metallic nickel and broad enhancement of intensity in the region from 854.8 to 859.5 eV as compared with the spectrum of unreacted nickel.

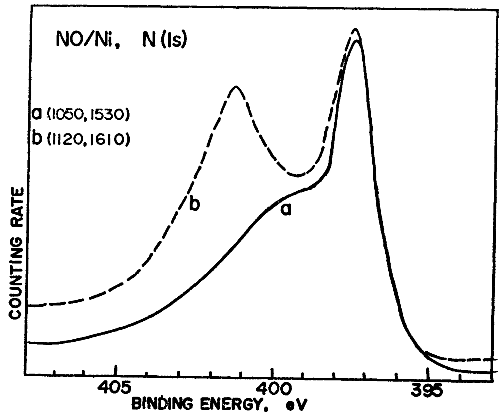

Fig. 4. N(1s) peaks from evaporated nickel exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min.

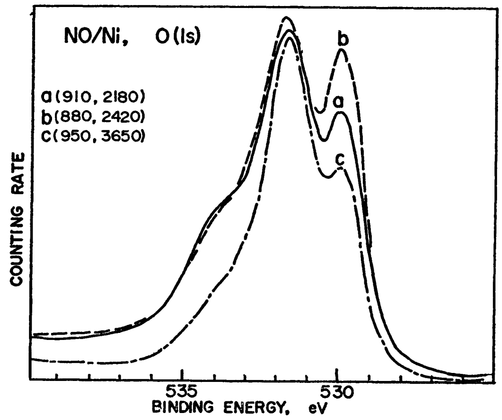

Fig. 5. O(1 s) peaks from evaporated nickel exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min, (c) 20 Torr of air for 5 min.

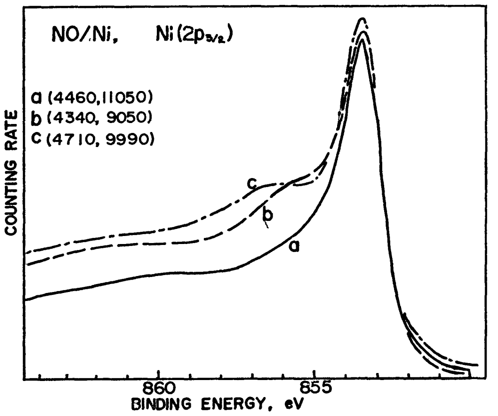

Fig. 6. Ni($2p_{3/2}$) peaks from evaported nickel exposed to (a) 5 Torr of NO for about 1 s, (b) 10 Torr of NO for 10 min, (c) 20 Torr of air for 5 min.

Spectra b of Figs. 4 to 6 were recorded after evaporated nickel was exposed to NO at a pressure of 10 Torr for 10 min. The N(1s) peaks are at 397.6 and 401.3 eV. Three O(1s) peaks are at the same binding energies as those in spectrum a. A shifted Ni($2p_{3/2}$) peak is clearly shown at 855.9 eV; 2.4 eV from metallic nickel.

Spectra c of Figs. 5 and 6 were observed after evaporated nickel was exposed to air at a pressure of 20 Torr for 5 min. The binding energies of three O(1s) peaks are the same as those of spectra a and b. The chemical shift of Ni($2p_{3/2}$) peak of oxidized nickel

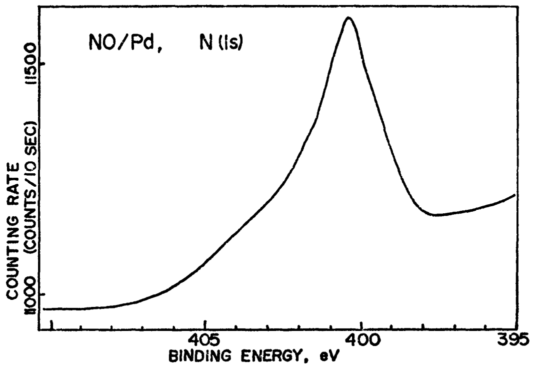

Fig. 7. N(1s) peaks from evaporated palladium exposed to 10 Torr of NO for 10 min.

is larger by 0.5 eV than that obtained when nickel was exposed to NO. After this surface oxide was subsequently exposed to NO at a pressure of 10 Torr for 10 min, no N(1s) peak could be detected even after counting the photoelectrons for 10 s/channel.

Figure 7 shows the N(1s) spectrum when evaporated palladium was exposed to NO at a pressure of 10 Torr for 10 min. The peak is at 400.4 eV and a very weak shoulder around 403.5 eV. The Pd 3d spectrum was the same in shape as that for unreacted palladium and no new peak was observed. The Pd($3p_{3/2}$) electrons give a strong peak at 532.7 eV and make the O(1s) peaks indistinct. The shape of Pd($3p_{3/2}$) peak is almost the same as that for unreacted palladium; indicating a low counting rate for O(1s) peaks.

When evaporated palladium was exposed to NO at a pressure of 5 Torr for about 1 s, the intensity of N(1s) peak at 400.4 eV was two thirds of that in Fig. 7 and the 403.5-eV shoulder could not be detected.

Discussion

The results for evaporated iron, nickel, and palladium reacted with NO show two or more N(1s) peaks (Table 1). The binding energy of N(1s) in NO_3^- or NO_2^- of $NaNO_3$(407.4 eV), $NaNO_2$ (404.1 eV), or of their transition metal compounds is much larger[8] than that obtained from the reaction of NO with the metals except the 403.5-eV peak in case of palladium. The N(1s) peaks from 400.2 to 402.5 eV for the surface species correspond in binding energy well with those in transition metal nitrosyls whose binding energies lie between 399.6 and 403.3 eV[8,9] and these peaks are, therefore, assigned to surface NO species.[10] The decrease in intensities of these peaks during spectra measurement is due to NO desorption occurred probably by evacuation or ejected electrons on the surface.

The N(1s) peaks at 396.6 eV for iron and 397.6 eV for nickel are smaller by 2.0 eV or more than that of NO^- in the metal nitrosyls. These peaks are reasonably assigned to the surface nitride since the N(1s) binding energies of VN and CrN are 397.2 and 396.6 eV, respectively.[8] The dissociation of NO on nickel has been reported.[4,5] The above results indicate that the dissociated nitrogen are in part present in the surface compounds on iron and nickel without recombining nitrogen molecule. From the N(1s) binding energies, the nitride-nitrogen is likely to be more ionic (negative) on iron than on nickel. This is similar to that the main oxygen species is smaller by 1.7 eV in binding energy of O(1s) peak (namely, more negative) on iron than on nickel when exposed to air. The absence of the nitride peak in case of palladium shows quite different reactivity to NO from nickel and indicates less stability of nitride or oxide on palladium surface at room temperature.

When iron and nickel were exposed to NO, the strongest O(1s) peak is at 530.0 eV in case of iron (Fig. 2) and at 531.7 eV in case of nickel (Fig. 5); being with the same binding energy as that obtained when each evaporated metal was exposed to air. In case of nickel exposed to air, the 531.7-eV peak does not correspond to the O(1s) of NiO (530.0 eV) and has been assigned to the surface oxide[11] or Ni_2O_3.[12] These facts also indicate that a large amount of oxygen anions are present on iron and nickel as a result of the dissociative reaction of NO.

When iron was preoxidized by air, the N(1s) due to

Table 1. Nitrogen 1s binding energies and NO stretching frequencies

Samples		N(1s) B. E., eV	ν(NO), cm^{-1}	
$Na_2[Fe(NO)(CN)_5]2H_2O$		403.3[9]	1939[18]	
$[FeCl(NO)(diars)_2](ClO_4)_2$		402.9	1865[15]	
$[Fe(NO)(diars)_2](ClO_4)_2$		401.2, 399.6	1760[14]	
$[FeCl(NO)(diars)_2]ClO_4$		400.0	1620[14]	
$NiCl(NO)[P(C_6H_5)_3]_2$		399.8	1735[17]	
$Ni(N_3)(NO)[P(C_6H_5)_3]_2$		399.6		
$RuCl(NO)_2[P(C_6H_5)_3]_2PF_6$		402.6, 400.2	1845, 1687[13]	
VN		397.2[8]		
CrN		396.6		
Surface Species	NO/Fe	a) 400.7, 396.6	1810[4]	1805[2]
		b) 401.0, 396.6 402.5	1720	1375
	NO/Ni	a) 400.2, 397.6	1840[4]	1850[2]
		b) 401.3, 397.6	(2205)	1735
	NO/Pd	400.4, (403.5)	1845, 1765[3]	

a) NO exposure; 5 Torr for 1s. b) NO exposure; 10 Torr for 10 min.

the nitride could not be detected (Fig. 1-d). This indicates that the NO dissociation is effective on metal surfaces but not on the surface oxides.

The O(1s) peak at 533.5 eV in case b of Fig. 2 shows a fairly strong intensity and, under this reaction condition, the N(1s) peak at 401.0 eV is quite strong (case b of Fig. 1). Moreover, a weak O(1s) peak appeared at 533.7 eV (d of Fig. 2) with the appearance of the N(1s) peak at 401.3 eV (d of Fig. 1) when preoxidized iron surface was exposed to NO. These results indicate that the O(1s) at 533.5 eV and the N(1s) at 401.0 eV come from the same NO species. This is also affirmed by the counting rate ratio of the O(1s) and N(1s) peaks. The ratio of O(1s) peak to N(1s) peak in $NaNO_3$ is namely 1.2 per atom. In cases b of Figs. 1 and 2, the ratio is 1.25 for the O(1s) at 533.5 eV to the N(1s) at 401.0 eV.

In case of nickel, the O(1s) peak at 533.5 eV appears even when evaporated nickel was exposed to air (c of Fig. 5). This weak peak has been proposed as atomic oxygen adsorbed on nickel.[12)]

In cases of iron, the ratio of NO to oxygen anion is derived approximately as 0.23 (case a) and 0.64 (case b), respectively, from the intensity ratio of the O(1s) peaks around 533 eV to the one at 530.0 eV of Fig. 2. This indicates that the initial reaction of NO with iron is, in larger part, the dissociative. Also from the intensity ratios of the N(1s) at 396.6 eV was the O(1s) at 530.0 eV in Figs. 1 and 2 and the counting ratio, 1.2, of O(1s) to N(1s), roughly 1/3 (case a) and 1/5 (case b) of nitrogen atoms formed by NO dissociation are estimated to remain on iron surface without recombining into molecular nitrogen. In other words, the proportion of the surface species is roughly, 15 NO: 65 O: 20 N in case a and 35 NO: 55 O: 10 N in case b.

In case of nickel, the corresponding values are roughly 7 : 65 : 28 (case a) and 10 : 75 : 15 (case b) which were estimated from the intensity ratio of the N(1s) at 400.2 eV (case a) or 401.3 eV (case b) for NO, the O(1s) at 530.1 eV plus the O(1s) at 531.7 eV for O, and the N(1s) at 397.6 eV for N.

When evaporated iron was exposed to air at a pressure of 20 Torr for 5 s, iron surface was oxidized nearly to Fe(III) as evidenced by the chemical shift, 4.0 eV, for Fe ($2p_{3/2}$) peak (Fig. 3-c) since that of Fe_2O_3 is 4.2 eV.[6)] In case b of Fig. 3, the iron surface was oxidized by exposure to NO approximately to the same depth as in case c as shown by the similar intensity ratio of the two Fe($2p_{3/2}$) peaks which come from unreacted and oxidized iron in both cases. However, the chemical shift in case b is 3.0 eV and smaller by 1.0 eV than that in case c. This indicates that the iron atom on the surface is with higher electron densities in case b than in case c.

In case of nickel, the chemical shift of Ni($2p_{3/2}$) is also smaller when exposed to NO (2.4 eV in Fig. 6-b) than when exposed to air (2.9 eV in c). This also indicates that a surface nickel atom is with higher electron densities when reacted with NO than when oxidized with air.

Blyholder and Allen[4)] have explained variations in NO stretching frequencies of the chemisorbed NO by the amount of charge in the second lowest π orbital of the Ni-N-O system, antibonding for the N–O bond but bonding for the Ni–N bond, which is depending on the number of metal atoms around the metal atom to which the chemisorbed NO is bound. In cases of iron and nickel, however, the surface oxygen and nitrogen anion as ligands are expected to take more important role in variations of NO stretching frequencies when considering the present photoelectron data, namely, the extent of surface oxidation and the proportions NO, O, and N on the surfaces. In $\{RuCl(NO)_2[P(C_6H_5)_3]_2\}PF_6$ complex, two different types of nitrosyls are bonded to the same metal atom;[13)] linear equatorial nitrosyl (N(1s): 402.6 eV,[9)] NO str. freq.: 1845 cm^{-1} [13)]) and apical bent nitrosyl (400.2 eV, 1687 cm^{-1}). The surface compounds on the metal which have mixed ligands (NO, O, N) will also have various coordination geometries, coordination numbers, and electronic states. The metal atom surrounded by larger number of oxygen or nitrogen anions, especially oxygen, draws electrons from the NO to larger extent and gives higher binding energy of N(1s) peak and higher frequency of NO band as discussed below. Among the metal nitrosyls, bent nitrosyls (formally NO^-) generally show low binding energy of N(1s) peak and linear nitrosyls (NO^+) can show either low or high binding energy peak depending on the extent of π back-bonding from the metal.[9)] The N(1s) binding energies are expected to be correlated with NO stretching frequencies in metal nitrosyls since the high positive charge on NO means less electrons on the orbital which is antibonding for the NO bond and, consequently, higher NO frequency. Such but rough correlations have been reported for many nitrosyl complexes.[9)] For the iron complexes listed in Table 1, a good correlation is shown between the N(1s) binding energies and the NO stretching frequencies. The NO groups have been concluded to have relatively high positive charges in the upper two complexes and negative charges in the fourth complex. For the surface NO groups, the N(1s) of 401.0 eV and the NO str. freq. of 1720 cm^{-1} [4)] correspond to the 401.2 eV[9)] and the 1760-cm^{-1} [14)] for $[Fe(NO)(diars)_2](ClO_4)_2$ and the 402.5 eV and the 1810-cm^{-1} to the 402.9 eV and the 1865 cm^{-1} [15)] for $[FeCl(NO)(diars)](ClO_4)_2$. This means that the positive charges on NO groups increase and, namely, the π back donation to the NO decrease as NO oxidizes iron surface to larger extent as a result of dissociative reaction and the surface NO species increase in number.

The intensity of 401.0-eV peak is stronger than that of the 402.5 eV peak in case b of Fig. 1 while the the intensity of the 1720-cm^{-1} band is weaker than that of the 1810-cm^{-1} band for evaporated iron particles in an oil exposed to 10 Torr for NO 1 hr.[4)] In the experiment by Terenin,[2)] the 1805-cm^{-1} band shows approximately the same intensity as the 1735-cm^{-1} band for dispersed iron on alumina exposed to 20 Torr NO. This may suggest that the infrared bands were obtained the sample which was oxidized to larger extent by the dissociative reaction of NO and was bonded by larger number of NO species than the present photoelectron peaks were. The *trans*-[FeCl-

$(NO)(diars)_2](ClO_4)_2$ underwent decomposition in the X-ray beam, as evidenced by a gradual growth of a 400.4 eV peak at the expense of the 402.9 eV peak.9) Such phenomenon also explains the intense 401.0 eV peak for the surface NO species.

The N(1s) binding energy for the chemisorbed NO on nickel is 400.2 eV (case a) and 401.3 eV (case b). The former value is near to that in $NiCl(NO)[P(C_6H_5)_3]_2$ (399.8 eV) and $Ni(N_3)(NO)[P(C_6H_5)_3]_2$ (399.6 eV,9) Ni–N–O angle: 152.7°16)). The NO frequency in $NiX(NO)[P(C_6H_5)_3]_2$ (X=Br, I) is 1735 cm^{-1}.17) The weak 1735-cm^{-1} band for chemisorbed NO2) seems to correspond to the surface NO species giving 400.2 eV peak. The low binding energy of N(1s) suggests a small negative charge on the surface NO. 401.3 eV peak in case b indicates less electron donation to NO from the nickel atom at higher oxidation state and is presumably associated with the NO giving the 1840-cm^{-1} band4) (or 1850-cm^{-1} band2)).

The low binding energy of N(1s) peak (400.4 eV) in case of palladium suggests that the surface NO groups bond to the palladium atom at very low oxidation state. This is in accord with the facts that the intense O(1s) peak was absent and no new peak for O (3d) due to oxidized palladium was detected. The surface NO may have small negative charge on it. Strongly chemisorbed NO on palladium supported on silica gives bands at 1845 and 1765 cm^{-1}.3) However, the correspondence of the photoelectron peaks with the infrared bands is uncertain at present.

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References

1) Recent reviews, a) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966), b) J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 385 (1967), c) N. G. Connelly, *Inorg. Chim. Acta Rev.*, **6**, 47 (1972).

2) L. M. Roev and A. M. Terenin, *Optika Spektrosk.*, **7**, 756 (1959).

3) H. Dunken and H. Hobert, *Z. Chem.*, **3**, 398 (1963).

4) G. Blyholder and M. C. Allen, *J. Phys. Chem.*, **69**, 3998 (1965).

5) W. M. H. Sachtler, Actes Congr. Intern. Catalyse, 2nd, Paris (1960), p. 2197 (1961).

6) K. Kishi and S. Ikeda, This Bulletin, **46**, 341 (1973).

7) Y. Baer, P. F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **1**, 55 (1970).

8) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

9) P. Finn and W. L. Jolly, *ibid.*, **11**, 893 (1972).

10) In order to check the energy references of Jolly *et al.* and of us, we measured the binding energy of N(ls) in $NaNO_3$ and KCN as common samples. Their binding energies are 407.4 (407.7) eV and 399.0 (398.7) eV, respectively. Our data are shown in the parentheses. This proves that a direct comparison of our data with those by Jolly *et al.* is possible without any correction.

11) G. Schön and S. T. Lundin, *J. Electron Spectrosc.*, **1**, 105 (1972/73).

12) K. S. Kim and R. E. Davis, *ibid.*, **1**, 251 (1972/73).

13) C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4760 (1970).

14) W. Silerthorn and R. D. Feltham, *Inorg. Chem.*, **6**, 1662 (1967).

15) R. D. Feltham, listed in Ref. 9 as private communication to Prof. W. L. Jolly.

16) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

17) R. D. Feltham, *ibid.*, **3**, 116 (1964).

18) G. Paliani, A. Poletti, and A. Santucci, *J. Mol. Struct.*, **8**, 63 (1971).