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Infrared Reflection Study of NO Chemisorption on Evaporated Nickel and Palladium Films

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The chemisorption of NO on evaporated Ni and Pd films was investigated by means of ir reflection and flash desorption spectroscopy. NO is nondissociatively adsorbed at all coverages on Pd films, but initial dissociation of NO molecules occurs on Ni films followed by molecular adsorption. A band at 1805 cm^{-1} and a pair of broad bands at 1860 and 1750 cm^{-1} have been assigned to monomer and dimer species, respectively. This was confirmed by the band shifts of isotopically substituted ^{15}NO molecules and flash desorption measurements. Adsorbed *cis* dimers are oriented with the molecular plane normal to the metal surface.

1. INTRODUCTION

Although the reaction of nitrogen monoxide with metal surfaces has become a topic of great interest in catalytic chemistry in connection with air pollution, only a few systematic studies of this molecule adsorbed on clean surfaces have been reported. We have investigated NO chemisorption on deposited metal surfaces using infrared reflection spectroscopy which can produce direct information on the geometric arrangement and orientation of the adsorbed species with respect to the surface. In this paper, we report infrared reflection studies of NO adsorption on deposited Ni and Pd films. The results basically confirm previous results (*1*) which indicated that, while NO chemisorbed mainly as *cis*-dimer species for high coverages at room temperature, it formed monomer species at low coverage on Ni films. We obtained similar results for the Pd films, except that initial dissociation did not occur on this metal. The suggested band assignments were confirmed by the isotope shift of the absorption bands. The change in band intensities was examined using cleaved NaCl with a stepped surface and cleaved mica with a smooth surface as the film support.

2. EXPERIMENTAL

The UHV ir cell and full experimental procedures will be described elsewhere (*2*). The spectrometer (IR-G, Nihonbunko, Ltd.) was operated in a double beam mode and the absorption due to atmospheric water vapor could nearly be compensated for by the use of a reference cell. To obtain sufficiently measurable signals, a signal enhancement procedure was used, which involved repetitive scanning of the spectrum followed by computer signal averaging.

Thermal desorption was monitored by using a quadrupole mass spectrometer (NEVA-515). The metal film was heated by radiation from a tungsten filament with a heating rate of 5°/min after infrared reflection measurements.

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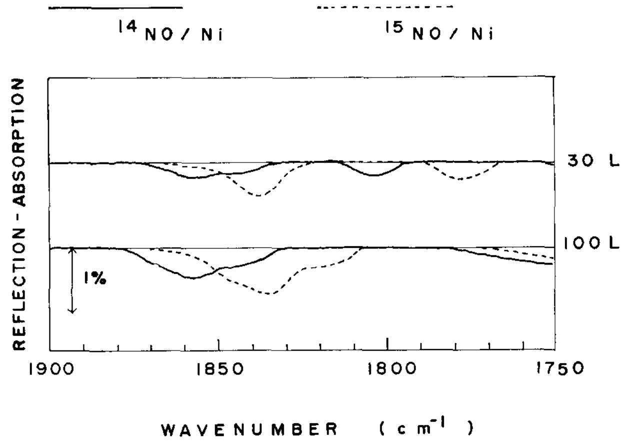


FIG. 1. Infrared reflection spectra of chemisorbed ^{14}NO and ^{15}NO on deposited Ni film at room temperature.

Nickel and palladium were evaporated by resistively heating wires (3N, 1 mm Ni; 4N, 1 mm Pd; from Wako Chemical Co., Ltd.) and the films were deposited on polished quartz glass. A background pressure in the low 10^{-9}-Torr range (1 Torr $=133.3$ N m^{-2}) could be routinely obtained, but it rose to 6×10^{-9} Torr during film deposition. High-purity NO gas (99% from Takachiho Co., Ltd.) was used.

3. RESULTS

3.1. Chemisorption on Ni

The absorption spectrum at room temperature of NO adsorbed on a nickel film deposited at 300°K is shown in Fig. 1. No absorption band was observed until a 10-L dose (1 L $=10^{-6}$ Torr-sec) had been admitted into the cell, showing initial dissociative adsorption. Upon further NO admission, a weak absorption band appeared around 1805 cm^{-1}. As the NO dose was increased to 30 L, another absorption band began to grow at around 1860 cm^{-1}, with a shoulder on the low-frequency side. As the NO exposure was increased to 100 L, the 1860-cm^{-1} band developed to full intensity and a very broad band with weak intensity appeared at a lower frequency around 1750 cm^{-1}, while the intensity of the 1805-cm^{-1} band was reduced, or disappeared. Further NO doses did not increase the band intensities, suggesting the observed species should be at full coverage. The absorption bands around 1860 and 1750 cm^{-1} readily disappeared by heating the film to 100°C, while the peak at 1805 cm^{-1} recovered its original intensity. The former bands were absent as well upon adsorption at 100°C on an evaporated Ni film, and only the latter appeared. The bands at 1860 and 1750 cm^{-1} were broad and may be composed of more than one band, the fwhh being 25 cm^{-1}, whereas the 1805-cm^{-1} band was sharper with a fwhh of 10 cm^{-1} without a shoulder. The 1860-cm^{-1} band was the most intense one, although it was very difficult to estimate the intensity of the band at 1750 cm^{-1} because of the hindrance from features of water vapor in the spectrometer system. The intensity of the 1805-cm^{-1} band varied, depending upon the coverage and adsorption temperature.

The dotted lines in Fig. 1 represent the spectra of isotopically substituted ^{15}NO adsorption on a Ni film. Absorption bands are located at around 1840, 1780, and 1725 cm^{-1}, and correspond well with those for ^{14}NO adsorption.

3.2. Chemisorption on Pd

The general features of the spectra are very similar to the results on the Ni surface, as shown in Fig. 2. However, there are some important differences. NO did not dissociate at any exposure and was molecularly chemisorbed on the palladium film at room temperature. The bands began to appear at exposures of 2 L and reached their full intensity after an exposure of 10 L. The intensity of the band at 1805 cm^{-1} remained nearly constant during the whole stage of adsorption, though on Ni film this band drastically reduced in intensity or disappeared. The band at 1855 cm^{-1} shifted slightly to 1860 cm^{-1} and increased in intensity until it was saturated after admission of 10 L NO. As with the results on nickel films, this band was very broad and appeared to be composed of two or more bands. Also in agreement with the results on the nickel surface, the only band observed at high temperatures was that appearing at 1805 cm^{-1}. Adsorption of isotopically substituted ^{15}NO on a Pd film was also studied in order to confirm the band assignment. Each band shifted to lower frequencies by 25–30 cm^{-1}, which is in fair agreement with previous transmission results (*3*).

3.3. Flash Desorption Results

After infrared reflection measurements the metal film was heated by radiation from a tungsten filament with a heating rate of 5°C/min. Figure 3 shows the NO desorption spectra from both Ni and Pd films. The peak maxima for both metals appeared at 80°C, and for the Ni film there occurred a shoulder on the high-temperature side of the main peak, whereas for Pd no shoulder was observed. A very small peak around 250°C (for the Ni film) was observed, although it seems likely that this was due to the desorption from the cell walls, or from the other elements in the chamber. These NO peaks were observed in both the spectra of mass number 30 (^{14}NO) and 31 (^{15}NO).

3.4. Orientation of $(NO)_2$ Dimer and Monomer

The Ni film was prepared by deposition onto a well-ground quartz glass plate which was held on a copper support, this technique enabling the production of fairly

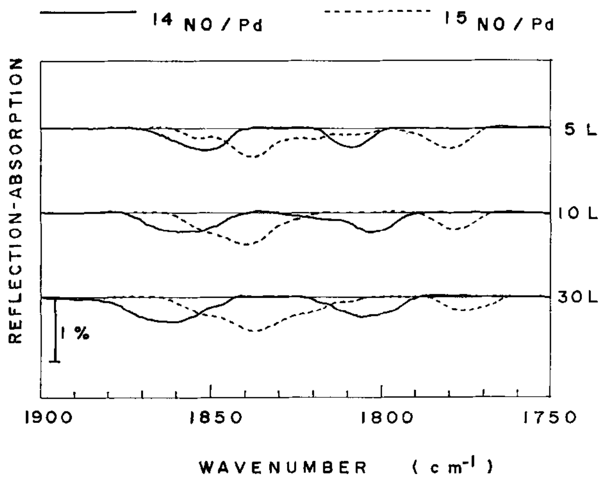


FIG. 2. Infrared reflection spectra of chemisorbed ^{14}NO and ^{15}NO on deposited Pd film at room temperature.

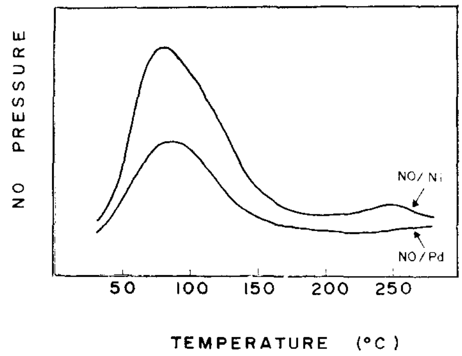


FIG. 3. Flash desorption spectra.

flat surfaces. A roughened surface could be obtained by using cleaved NaCl as the support, which had steps of the order of microns. Another smooth surface could be prepared by using cleaved mica as the support. Figure 4 shows the results of NO adsorption on nickel films evaporated on smooth and rough supports at room temperature and at full coverages (100 L of NO). The top spectrum is that of a transmission infrared study of NO chemisorbed on silica supported chromium, reported by Kugler and Gryder (*3*). In the transmission spectrum the antisymmetric stretching band of the *cis*-$(NO)_2$ dimer (1750 cm^{-1}) is five times as strong in intensity as the symmetric stretching band, whereas the reflection spectra show the reverse intensity relationship because of the surface selection rules operating in reflection spectroscopy as described below. The weak, broad absorption band due to antisymmetric stretching of the $(NO)_2$-dimer species which did not appear on the smooth film surfaces at high coverages could be observed when the cleaved NaCl having a large stepped surface was used as the film support.

4. DISCUSSION

4.1. Dimer and Monomer Chemisorption

The infrared reflection spectra revealed two kinds of absorption bands. The 1805-cm^{-1} band which appeared at an early stage of adsorption and disappeared at high coverages on the nickel surface is assigned to the N–O stretching vibration of the monomer species. The broad bands at 1860 and 1750 cm^{-1} can be assigned to the *cis*-$(NO)_2$ dimer species since they increased in intensity at high coverage and were easily removed by heating, and their

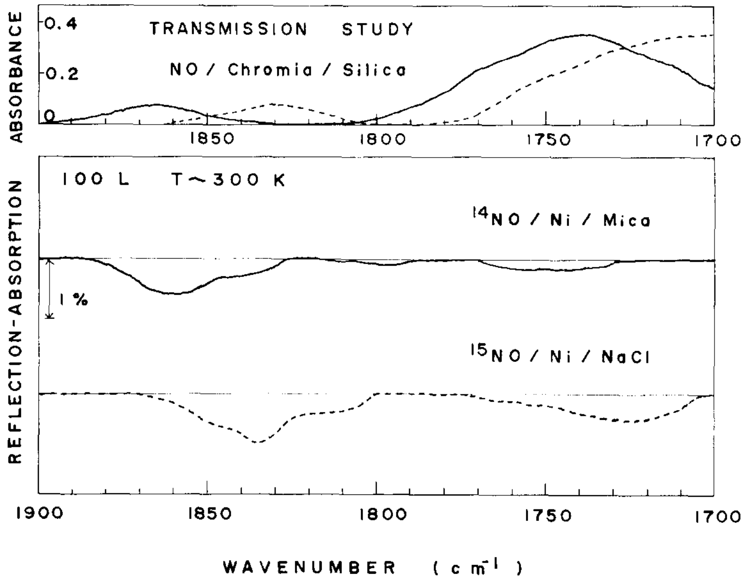
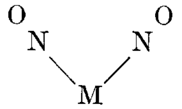


FIG. 4. Infrared reflection spectra of chemisorbed NO on rough and smooth surfaces.

frequencies resembled those of the neutral *cis*-$(NO)_2$ molecule in a matrix, which appear at 1860 (symmetric stretching) and 1765 cm^{-1} (asymmetric stretching). The twin-type NO,



species instead of dimer species could explain the above band assignments, as many workers have deduced (*4*). However, recent ELS results (*5*) of NO chemisorption on Ni(111) support our dimer $(NO)_2$ model.

The stretching frequencies of the $(NO)_2$ dimer species shift only slightly upon adsorption, which indicates that the interactions between the dimer species and the metal surface are relatively weak. The flash desorption results indicate that the majority of NO molecules desorb at temperatures less than 100°C and could explain why the absorption bands due to the dimer species could not be observed at high temperatures.

On the other hand, the band at 1805 cm^{-1} appeared at a relatively earlier stage of adsorption (at low coverages) and remained at high temperatures (up to 100°C). Kugler and Gryder (*3*) investigated infrared spectra of NO adsorbed on silica-supported chromia, observing three bands between 1900 and 1600 cm^{-1}, and ascribed two paired bands at 1862 and 1780 cm^{-1} to the adsorbed $(NO)_2$ dimers, since the frequency and the intensity of the two bands are very similar to the dimer $(NO)_2$ molecule, and assumed the remaining 1800-cm^{-1} band was due to the nitric oxide adsorbed on the surface. The results of the present investigation are in good agreement with their transmission studies, except for the band intensities which will be discussed later. From these facts, the 1860- and 1750-cm^{-1} bands can be assigned to the dimer $(NO)_2$ symmetric and antisymmetric stretching vibrations, respectively, and the 1805-cm^{-1} band to the monomer NO species.

TABLE 1

Observed and Calculated Frequencies of the Dimer and the Monomer Bands[a]

	Obs.	Obs.	Calc.
Monomer	^{14}NO	^{15}NO	^{15}NO
	1805	1780	1773
Dimer	$(^{14}NO)_2$	$(^{15}NO)_2$	$(^{15}NO)_2$
Sym.	1860	1840	1827
Asym.	1750	1725	1719

[a] Unit: cm^{-1}.

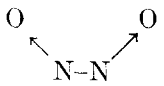
The frequencies of the $(^{15}NO)_2$-dimer bands of chemisorbed species are roughly calculated (*3*) by using the values of force constants obtained from the bands at 1860 and 1750 cm^{-1} in the ^{14}NO spectrum. The results are shown in Table 1. The monomer band shift is easily calculated and is also shown in the table. The agreement with the observed value is good, suggesting that the band assignments of these species are correct.

Although the frequency of the dimer NO stretching vibration bands shift very slightly from those of the gaseous dimer molecules, the frequency of the NO monomer stretching vibration is considerably lower than for gaseous NO (1875 cm^{-1}). A nitrogen–metal bond involving $d\pi$–$p\pi^*$ backdonation of electrons from the *d* orbitals of the metal into the antibonding orbital of the NO molecule reduces the NO bond strength and therefore explains the lowering of the NO stretching frequency. The adsorbed dimer species desorb as NO monomer, giving only one NO desorption peak from the palladium film with the same peak temperatures as for the nickel film, but in the latter case the peak was accompanied by a shoulder on the high-temperature side which may be due to desorption of chemisorbed NO monomer species.

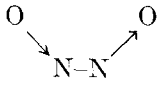
The fact that only a single desorption peak was obtained from the Pd surface, whereas the infrared spectrum exhibited two bands, may suggest that the binding energy of the chemisorbed dimer and monomer species is very similar. Hence it would be difficult to resolve the differences by thermal desorption. In the case of nickel, the binding energies may be rather different, which would explain the shoulder on the high-temperature side of the peak. The position of the metal mirror shifted slightly at temperatures higher than 100°C, and the disappearance of the monomer infrared band could not be observed.

4.2. Orientation of cis-$(NO)_2$ Dimer on Metal Surfaces

In infrared reflection spectroscopy, the oscillating electric field at the metal surface is predominantly perpendicular to the mirror surface. Therefore, it can only interact with the vibrational mode accompanying the dipole moment change which has a sizable component perpendicular to the surface. Thus, the orientation of the adsorbed species in relation to the macroscopic metal surface can be determined by analyzing the relative intensities of the bands. The dimer $(NO)_2$ molecule has two absorption bands at 1860 and 1788 cm^{-1} (*6*), and the former is assigned to the symmetric



stretching vibration, in which the dipole moment change is parallel to the principal axis (C_2) of the molecule, and the latter to the antisymmetric



vibration, in which the dipole moment change is perpendicular to the axis. Therefore, the dipole moment change parallel to the C_2 axis of the molecule, namely, the symmetric N–O stretching vibration, should interact with the oscillating field and result in a strong band in the reflection spectra, provided the C_2 axis of the dimer molecule is normal to the surface. The antisymmetric mode, on the contrary, would not interact with the infrared radiation and the corresponding band should be missing in the reflection spectra. The transmission results indicate that the intensity of the antisymmetric N–O band is five times that of the symmetric one on supported fine metal particles. The complete reversal of the intensity relation or sometimes the absence of antisymmetric mode indicates that the dipole moment change of the antisymmetric mode of vibration is parallel to the mirror surface, while the dipole moment change of the symmetrical vibration is perpendicular to the surface and results in a strong band.

Since the cleaved NaCl single crystal is stepped, the deposited metal surface on this support is probably rough, whereas the deposited films on mica support may be smooth. The change in the intensities of the antisymmetric band in changing the surface, shown in Fig. 4, seems to reflect the surface roughness of the metal films evaporated onto the sodium chloride plates since the orientation of the molecules adsorbed on the surface will be relatively random to the macroscopic surface of the film.

4.3. Comparison with Other Techniques

Recently, high-resolution electron-energy-loss spectroscopy (ELS) has reached the stage where it is possible to measure the surface vibrations of chemisorbed species on clean surfaces (*7*). Since the selection rules for infrared reflection spectroscopy and ELS appear to be the same, the two techniques can be compared. Ibach observed that at low coverages of NO on a Pt(111) single crystal the NO monomer was the dominant surface species and as the coverage was increased the population of the monomer decreased, as it was converted to the dimer species. He reported that there existed a phase transition between the two species, which is in accord with the results reported in the present and a previous papers (*1*). Studies of NO adsorption on Ni(111) by LEED, AES, UPS, and flash desorption (*8*) have indicated that the dissociation of adsorbed NO started at 150°K and the resulting chemisorbed oxygen layer is converted, upon further increase of the oxygen concentration, into epitaxial NiO, while the nitrogen was desorbed as molecular nitrogen molecules. The results also indicated that NO forms two ordered structures, C(4 × 2)–NO and a hexagonal overlayer, from undissociatively adsorbed molecules, and that the densely packed hexagonal overlayer structure is more weakly bound to the surface than the C(4 × 2)–NO structure. The desorption was readily stimulated by electron irradiation, whereas the C(4 × 2)–NO structure was associated with a NO desorption maximum at 150°C in the flash desorption spectra. Accordingly, the 1805-cm^{-1} band which appeared at low coverage may correspond to the C(4 × 2)–NO LEED pattern species, while the prominent 1860-cm^{-1} band of the dimeric species may be due to hexagonally packed species adsorbed on NiO or Pd surfaces, since the band due to the former monomeric species was weak because of the small coverage and persisted in the reflection spectra in heating to 100°C, while the band due to the dimeric species was intense because of the large coverage and disappeared upon heating to about 100°C.

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