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NITROGEN MONOXIDE CHEMISORPTION ON EVAPORATED NICKEL SURFACE BY INFRARED REFLECTANCE SPECTROSCOPY

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Nitrogen monoxide chemisorbed on an evaporated nickel surface has been investigated by the IR high sensitivity reflection method combined with thermal desorption technique. The 1810 cm^{-1} band may be due to strongly chemisorbed monomer species on nickel surface, while the 1865 cm^{-1} be assigned to the weakly adsorbed dimer $(NO)_2$ species on the oxidized nickel surface.

Recently, the high sensitivity reflection spectroscopy1) using a multiple reflection or a single reflection technique has been successfully applied to the monolayer adsorption study of carbon monoxide on polycrystalline Ni2), W3) and noble metal surfaces4) or Cu single crystal surfaces5) under ultra high vacuum conditions. However, the great majority of works using this method have dealt almost exclusively with CO chemisorption probably because CO has an exceptionally intense absorption and the infrared bands of adsorbed species lie outside the atmospheric water vapor region.

We report here the first infrared reflection observation of NO molecules adsorbed on an evaporated nickel surface. The infrared study of NO molecule under UHV conditions has been rarely investigated so far, in spite of the fact that catalytic reactions of this molecule are of considerably practical interest.

The UHV IR cell and full experimental procedures will be described elsewhere.6) We used mainly the single reflection method in order to obtain thermal desorption results simultaneously. The spectrometer was operated in the double - beam mode and the absorptions of atmospheric water vapor could be nearly compensated by the reference cell.

Thermal desorption results were obtained 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 degrees per minute after infrared reflection measurement.

Nickel films were prepared by evaporating a nickel wire (4N8, 1 mmϕ from Schmidt Co., Ltd.) onto the polished quartz glass. The background pressure of the IR cell in the low 10^{-9} Torr. range could be routinely obtained, but rose to 6×10^{-9} Torr during film deposition. Nitrogen monoxide gas (high purity reagent grade gas (99.5 %) , Takachiho Co., Ltd.) was purified by distillation.

The room temperature adsorption of NO on a nickel film deposited at 300 K gave rise to absorption bands in the range from 1810 to 1870 cm^{-1} as shown in Fig. 1. After 10 L (1 L = 1×10^{-6} Torr sec) of NO admission (Fig. 1(a)), a weak absorption around 1810 cm^{-1} appeared, and no other peak was observed until the equilibrium pressure rose to 1×10^{-5} Torr. As the nitrogen monoxide pressure was increased to 1×10^{-4} Torr (Fig. 1(c)), the 1865 cm^{-1} band developed to full intensity while the intensity of the 1810 cm^{-1} band slightly decreased. This broad peak has a shoulder at low frequency side. These peaks did not reduce by pumping off at room temperature (Fig. 1(d)). The absorption bands around 1865 cm^{-1} easily disappeared by heating the substrate near 370 K but the peak at 1810 cm^{-1} was not extinguished until.370 K. High temperature adsorption (370 K) on a nickel film deposited at 300 K did not give the 1865 cm^{-1} band and only the 1810 cm^{-1} band appeared.

The prolonged exposure of nitrogen monoxide to the nickel surface showed a significant increases in the 14 and 28(m/e) mass peaks. The observed mass 28 peak probably arose from desorbed nitrogen molecules, since there were no infrared absorption bands in the CO absorption region. Figure 2 shows the NO desorption spectra. Two flash peaks were found; the higher temperature peak occurred at 400 K and the lower at 340 K with a heating rate of 5 degrees per minute (Fig. 2(a)). The exposure to NO at the elevated temperature of 370 K resulted in the appearance of only the higher temperature peak (Fig. 2(b)). It has less than 10 % of area of the lower temperature peak. Both peaks can be attributed to the desorption from the sample surface and not from the cell walls, the sample holder or the other elements in the chamber, because the background measurement without the sample mirror gave no substantial peak in these temperature regions. Accordingly, the higher temperature peak probably corresponds to the 1810 cm^{-1} infrared band which may be assigned to the monomer species and the lower temperature one to the 1865 cm^{-1} band of dimer species described below, respectively.

Kugler and Gryder7) have investigated infrared spectra of NO adsorbed on silica supported chromia. They observed 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 two bands are very similar to the dimer $(NO)_2$ molecule, and assumed the remaining 1800 cm^{-1} band to the monomer nitric oxide adsorbed on the surface.

In the present investigation, the reflection spectra showed the appearance of the only high frequency symmetric mode of the dimer and not the lower frequency antisymmetric mode. These results suggest that the $(NO)_2$ dimer adsorbs perpendicularly on the metal surface (Fig. 3), because the electric field at the metal surface is predominantly perpendicular to the mirror surface8) and it can interact with the vibrational mode in which the effective component of the dipole moment change is perpendicular to the surface.

The vibration frequency of the neutral $(NO)_2$ molecule in the gaseous state is 1860 cm^{-1}. Accordingly, the frequency of $(NO)_2$ dimer changes only slightly upon adsorption and indicates that interactions between dimer species and metal surface are very weak. Our previous study9) of NO chemisorption on iron deposited film showed a weak band near 1825 cm^{-1} . This band might be a monomer type species on oxide surface from the comparison with the nickel surface case.

The recent comprehensive investigation10) of NO on the Ni(111) surface by LEED, AES, UPS and flash desorption indicates that NO forms two ordered structures, C(4×2)-NO and hexagonal, from undissociatively adsorbed molecules. The dissociation of adsorbed NO starts at the temperature of 150 K and the resulted chemisorbed oxygen layer is converted, upon further increase of the oxygen concentration, into epitaxial NiO, while nitrogen desorbs as nitrogen molecules. The C(4×2)-NO structure is associated with a NO desorption maximum at 420 K in the flash desorption spectra, while the densely packed hexagonal overlayer structure

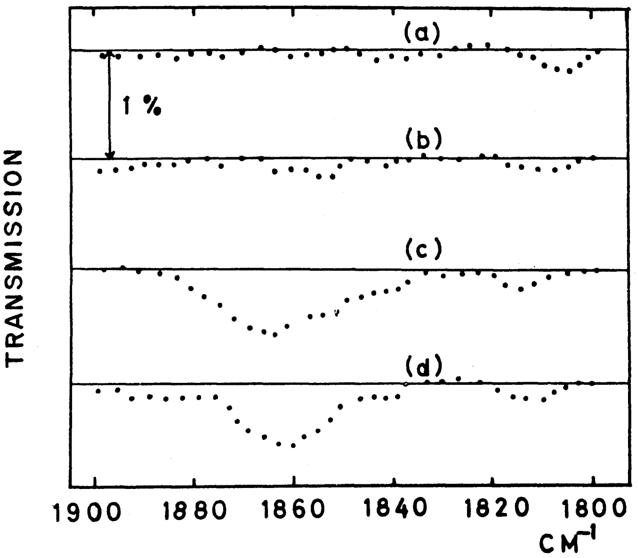

Fig. 1.
The high sensitivity reflection spectra of chemisorbed NO molecules on evaporated nickel surface. The evaporation and adsorption temperature is a room temperature.
(a) 10 L exposure of NO,
(b) 1×10^{-5} Torr equilibrium of NO addition,
(c) 1×10^{-4} Torr equilibrium of NO addition,
(d) room temperature evacuation to 1×10^{-8} Torr.

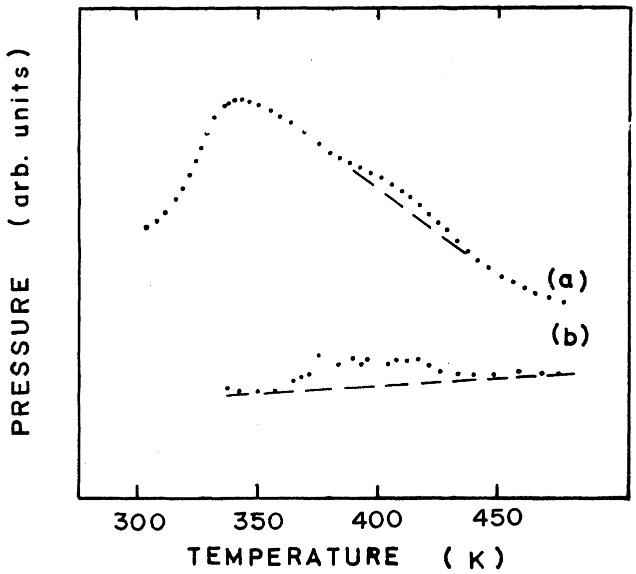

Fig. 2.
Flash desorption spectra for NO molecules.
(a) after admitting 1×10^{-3} Torr of NO and room temperature evacuation,
(b) after high temperature adsorption at 370 K and evacuation.
Ten-fold scale expansion was used.

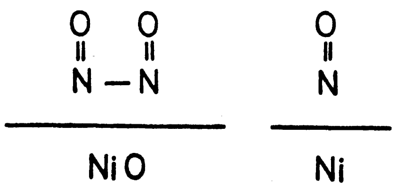

Fig. 3.
Illustration of orientation of adsorbed monomer and dimer species.

is more weakly bound to the surface than in the C(4×2)-NO structure and the desorption easily occurs by electron irradiation.

The 1810 cm^{-1} band appeared at low coverage may correspond to C(4×2)-NO LEED pattern species, while the prominent 1865 cm^{-1} band at high coverages may be due to hexagonal LEED pattern species adsorbed on NiO surface, because the former monomer type band showed only weak intensity due to the small coverage and persisted in heating up to 400 K, whereas the latter dimer species band was strong in intensity due to the large coverages and easily disappeared by heating near 370 K. A full account of the present results together with those from the epitaxially prepared single crystal nickel surfaces will be published later.

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