Adsorption and Dimer Formation of Nitrogen Monoxide on Pt(111) at Low Temperature

Jun Yoshinobu and Maki Kawai
The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako 351-01

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Adsorption and thermal reaction of NO on Pt(111) at temperatures from 25 K to 80 K have been studied by means of infrared reflection absorption spectroscopy. The physisorbed NO molecules form $(NO)_2$ species on the chemisorbed NO at low temperatures. There are at least two kinds of $(NO)_2$ species. The dimer species are decomposed into NO, which immediately desorbs above ~40 K. The remaining predominant species after 80 K heating is on-top linear NO species.

The adsorption and reaction of nitrogen monoxide (NO) on transition metal surfaces are of great scientific, technological and environmental interest. The chemisorbed states of NO on Pt(111) have been investigated by means of surface vibrational spectroscopy such as electron energy loss spectroscopy (EELS)[1,2] and infrared reflection absorption spectroscopy (IRAS).[3,4] These studies have shown that the chemisorbed states of NO on Pt(111) are coverage and temperature dependent.[1-5] However, since the temperature range in the previous studies has been limited above 80 K, only chemisorbed NO species have been investigated. In this letter, we report the adsorption and thermal reactions of NO on Pt(111) at temperatures from 25 K to 80 K using IRAS. In particular, we unambiguously show the formation of $(NO)_2$ on top of the chemisorbed NO layer from 25 K to 50 K.

The experiments were carried out in an ultrahigh vacuum chamber which was equipped with a three-grid retarding field analyzer for low energy electron diffraction and Auger electron spectroscopy, a quadrupole mass spectrometer for thermal desorption spectroscopy, and a pulsed gas doser. The base pressure was less than 1×10^{-10} Torr. The Pt(111) clean surface was prepared by Ar-ion bombardment, annealing, oxidation and flashing cycles. The sample was cooled down to 25 K by a cryo refrigerator and was heated up to 1400 K by electron bombardment from the rear. Gaseous NO was introduced onto the sample through a pulsed gas doser. The IRAS spectra were taken with a Fourier transform infrared spectrometer (Mattson RS-1) using an MCT detector. The Pt(111) clean surface is served as a background reference for an absorption spectrum. Each spectrum was obtained with 500 scans and 4 cm^{-1} resolution.

Figure 1 shows a series of IRAS spectra of adsorbed NO on Pt(111) at 25 K as a function of NO exposure. At 1.5×10^{14} molecules/cm^2, absorption bands are observed at 1691 and 1476 cm^{-1}. With increasing the exposure, the former band shifts to higher wavenumber and increases its intensity. On the other hand, the shape of the latter band broadens and its intensity decreases gradually. The observed band between 1690 cm^{-1} and 1710 cm^{-1} is assigned to on-top linear NO species, and the band between 1400 cm^{-1} and 1500 cm^{-1} is assigned to two-fold bridged NO species.[4] In addition to two kinds of chemisorbed NO species, two bands at 1860-1865 cm^{-1} and 1765-1780 cm^{-1} develop continuously with increasing the exposure. Thus, these bands are assigned to physisorbed species, which will be discussed in detail below.

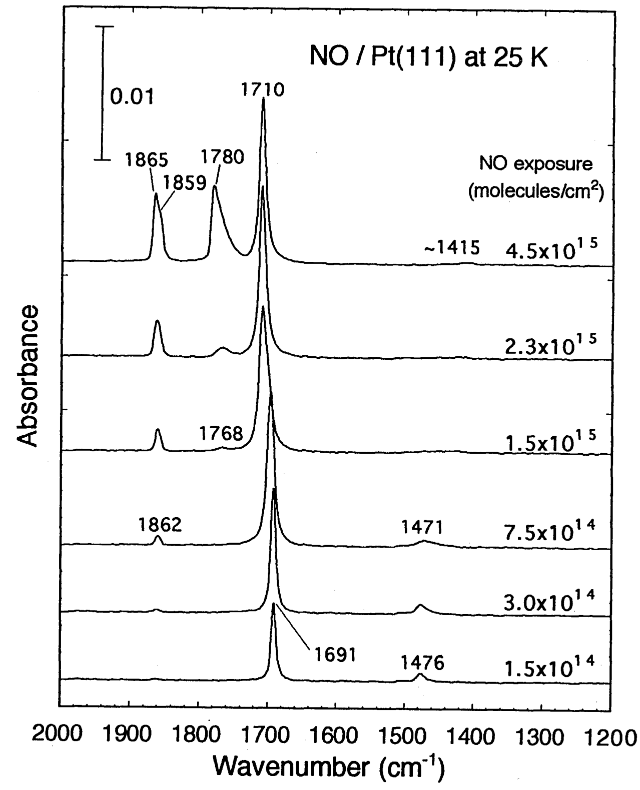

Figure 1. A series of IRAS spectra of NO on Pt(111) at 25 K as a function of exposure.

Figure 2 shows a series of IRAS spectra of adsorbed NO on Pt(111) as a function of heating temperature. Initially, a large amount of NO (the exposure = 4.5×10^{15} molecules/cm^2) was dosed on Pt(111) at 25 K, and the surface was heated to an indicated temperature and was quickly quenched to 25 K. At 25 K, in addition to chemisorbed NO, two bands are observed at 1865 and 1780 cm^{-1}. Note that both bands have shoulders at lower wavenumber sides. These two bands originate from $(NO)_2$ species. The symmetric and antisymmetric stretching vibrations of $(NO)_2$ are observed at 1860-1868 cm^{-1} and 1788-1789 cm^{-1}, respectively, in the gas phase,[6,7] and 1863-1866 cm^{-1} and 1760-1774 cm^{-1}, respectively, in the liquid and solid phases.[8] The observation of both symmetric and antisymmetric stretching vibrations indicates that the molecular plane of dimer should be tilted away from the surface normal. Ranke[9] has suggested the $(NO)_2$ formation in condensed layers of NO on Pt(111) at 20 K as concluded from the appearance of strong shake-up peaks in the O 1s and the valence band photoelectron spectra. The present IRAS study directly shows the the $(NO)_2$ formation on top of chemisorbed NO layer on Pt(111). The $(NO)_2$ formation has also been reported on Ag(111),[10,11] Pd(111),[12] and Nb(110)[13] at low temperatures.

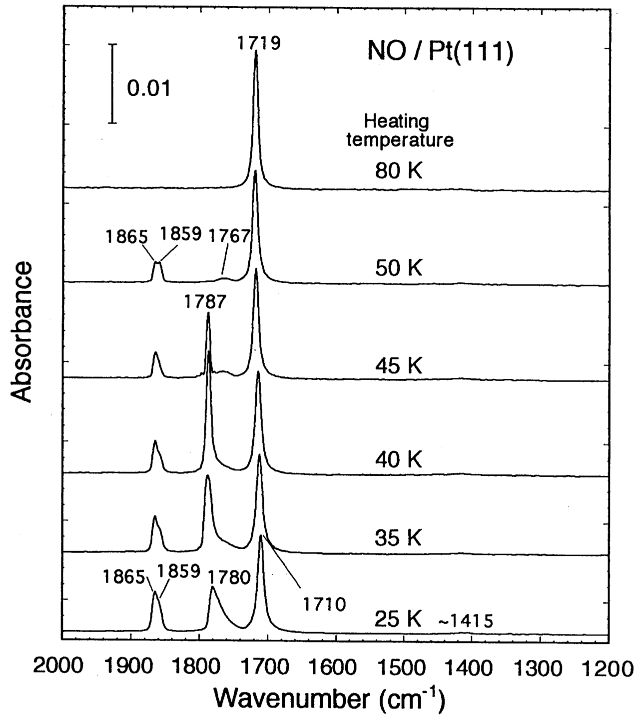

Figure 2. A series of IRAS spectra of NO on Pt(111) as a function of heating temperature. Each spectrum was taken at 25 K.

With increasing the temperature up to 40 K, the band is observed at 1787 cm^{-1} with an increased intensity and a sharper band width. This is interpreted to indicate that the dimer formation is developed by thermal activation. It is considered that some NO molecules adsorb randomly on top of the chemisorbed NO layer at 25 K. By heating the surface, these physisorbed NO species become mobile to form the dimer and the orientation may be ordered. Thus, the adsorbed state of $(NO)_2$ becomes more homogeneous. However, by heating to 45 K, the bands at 1865 cm^{-1} and 1787 cm^{-1} decrease their intensities. By heating to 50 K, the sharp band at 1787 cm^{-1} almost disappears, and the bands are observed at 1865, 1859, 1767 and 1719 cm^{-1}. The observation of two symmetric stretching vibrations (and also two antisymmetric stretching vibrations) indicates that there are two kinds of $(NO)_2$ species. The 1865 cm^{-1} and 1787 cm^{-1} bands are assigned to the condensed dimer species, and the 1859 cm^{-1} and 1767 cm^{-1} bands may be assigned to the dimer which adsorbs directly on top of the chemisorbed NO species. See also the spectra at medium exposures in Figure 1. In fact, thermal desorption of NO from physisorbed layers was observed with two desorption maxima at ~40 and 50 K. It is noted that no desorption of $(NO)_2$, NO_2, or O_2 was observed in the gas phase. Thus, by thermal activation above ~40 K, the physisorbed $(NO)_2$ species are decomposed into NO, which immediately desorbs from the surface. This results is consistent with the fact that the dimer is a stable form in the solid phase.[8] The change in intensity ratio between symmetric and antisymmetric stretching bands may be due to the change of orientation of $(NO)_2$ species on the surface during the ordering and desorption processes by heating.

A further heating to 80 K induces the complete desorption of physisorbed (multilayer) NO species. The remaining predominant species is on-top linear NO with a strong and sharp band at 1719 cm^{-1}, and a very small amount of two-fold bridged NO with a broad band around 1450 cm^{-1} also exists. It is noted that this spectrum is in agreement with that of saturated NO on Pt(111) at 80-160 K.[1-4]

The present IRAS study clearly proves the $(NO)_2$ formation over the chemisorbed NO layer on Pt(111) at low temperature.

References and Notes

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