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Adsorption and photoexcitation of NO on Ag/Pt(1 1 1)

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Abstract

The adsorption and photoreaction of NO on Ag films deposited on Pt(1 1 1) were investigated at 90 K by reflection-absorption infrared spectroscopy (RAIRS). Similar to Ag(1 1 1), NO molecules were found to be converted into $(NO)_2$ and N_2O on the Ag films. At an Ag thickness of 1 ML, however, a new adsorption state that reveals a RAIRS band at 1848 cm^{-1} is present on the surface. The $(NO)_2$ dimer species was found to react into N_2O, while the reaction of the new species was substantially suppressed. Upon photon irradiation with a wavelength of 193 nm, the three adsorption species on Ag(1 ML)/Pt(1 1 1) were depleted from the surface. The origin of the newly found species and the photoreaction mechanism are discussed.

Keywords: Infrared absorption spectroscopy; Nitrogen oxides; Platinum; Silver; Photon stimulated desorption (PSD)

1. Introduction

Formation of bimetallic substrates and interaction of molecules with such surfaces have been an interesting topic in recent years [1]. Bimetallic interfaces influence the molecular interaction and sometimes serve to improve the catalytic activity of the surface. A frequently used system is the combination of a transition metal and a noble metal [2].

On a (1 1 1) surface of a late transition metal such as Ni and Pt, NO molecules chemisorb at three-fold hollow and on-top sites [3–6]. On the other hand, NO molecules can interact only weakly with noble-metal surfaces where the inter-molecular interaction becomes important due to the unpaired electron of the molecule. On the Ag(1 1 1) surface, it is reported that the adsorbed NO forms a dimer $(NO)_2$ which reacts into N_2O [7–11]. A fundamental question is how the NO molecule interacts with a bimetallic surface of Ag/Pt(1 1 1). In the submonolayer regime, the CO adsorption was examined on Ag/Pt(1 1 1) where an increase of the binding energy of CO is reported [12]. Our first motivation is to clarify the adsorption state of NO on Ag/Pt(1 1 1) and examine the critical Ag thickness where the molecular interaction becomes bulk-like.

In a photoexcited process at a metal surface, a frequently discussed mechanism is that the photon excites an adsorbed molecule to a repulsive potential that causes significant energy transfer to nuclear motion leading to photodesorption or photodissociation [13–15]. In the usual case, however, such an electronically excited state origi- nating from the adsorbed molecule is in resonance with the bulk Bloch states spreading over the crystal, and the photoexcitation energy can not be localized at

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the molecular bond suppressing formation of a repulsive potential [16,17]. Alternative models taking into consideration the delocalized nature of the excited state are proposed [16,17]. The second motivation for the examination of molecular interaction with a bimetallic surface is evaluating the degree of localization of the photo excitation.

In the present paper, we report an experimental investigation of NO molecules adsorbed on Ag/Pt(1 1 1) by reflection–absorption infrared spectroscopy (RAIRS). The growth of Ag on Pt(1 1 1) has been intensively examined by scanning tunneling microscopy (STM) and is reported to take place in a layer-by-layer fashion at an appropriate temperature up to a thickness of 10 monolayers (ML) [18–21]. We present RAIRS data of NO adsorption for different Ag thicknesses. At a Ag thickness of 1 ML, we found a new adsorption state which can be assigned to either monomer or dimer species.

2. Experimental

The experiments were performed in a ultrahigh vacuum chamber (base pressure: 2.5×10^{-8} Pa) equipped with LEED and RAIRS. All RAIR spectra were acquired at a sample temperature of 90 K, which was achieved by liquid N_2 cooling. The Pt(1 1 1) substrate, 6 mm in diameter and 1 mm thick, was cleaned by repeated cycles of annealing at 1100 K in O_2 (3×10^{-5} Pa) and flashing to 1300 K. The cleanliness of the sample surface was checked by LEED and RAIRS that revealed appropriate absorption bands upon NO adsorption. The RAIRS measurements were performed using a conventional Fourier-transform infrared spectrometer equipped with an HgCdTe detector (Nicolet Magna 550). The absorption spectrum was averaged over 100 scans (acquisition time, 45 s) at a resolution of 8 cm^{-1}. For the photoexcitation experiment, ultraviolet photons from an excimer laser ($\lambda = 193$ nm) were introduced into the vacuum chamber through a CaF_2 window at a fluence of $\sim$1 mJ cm^{-2} and a repetition rate of 10 Hz. The NO adsorption was performed by backfilling the chamber. It is noted that higher dosageswere required to achieve saturation compared with previous studies [22–24], because the UHV chamber is designed such that the compartment for RAIRS is connected through a small tube to the main chamber where backfilled NO is partly pumped by the liquid N_2 reservoir. The deposition of Ag was conducted using a heated tungsten coil loaded with Ag wire at a sample temperature of 300 K, where Ag grows in a layer-by-layer fashion up to 10 ML [18]. In order to obtain a well-ordered film, the sample was annealed at 600 K after deposition, which is lower than the temperature for alloying to occur between Ag and Pt [18]. A slightly diffuse 1×1 LEED pattern was observed for Ag(10 ML)/Pt(1 1 1). The thickness of Ag was measured by a quartz oscillator placed beside the sample. After a series of RAIRS measurements for NO adsorption, the Ag film was removed by heating to 1300 K and the clean Pt(1 1 1) surface was recovered, as confirmed by NO absorption bands observed by RAIRS.

3. Results and discussion

Fig. 1 shows the coverage dependence of the RAIR spectrum for NO adsorbed on Ag(0.2 ML)/Pt(1 1 1) at a sample temperature of 90 K. With an NO dosage of 4 L, absorption bands are observed at 1490 and 1700 cm^{-1}. As the NO dosage is increased to 8 L, the absorption band at 1700 cm^{-1} increases in intensity while the band at 1490 cm^{-1} disappears. This behavior is exactly the same as that observed for the pure Pt(1 1 1) surface indicating that the two bands at 1490 and 1700 cm^{-1} correspond to the stretching vibration of NO adsorbed at three-fold hollow and atop sites of Pt(1 1 1), respectively [5,6,22].

Further dosage of 100 L yields additional absorption bands at 1254, 1855, and 2227 cm^{-1} in the RAIR spectrum, which originate from the species adsorbed at the surface of deposited Ag. After annealing the surface at 120 K, these three bands vanish while the one at 1710 cm^{-1} remains indicating thermal desorption and/or decomposition of the corresponding species. This result suggests that NO is more strongly bound on Pt(1 1 1) than the Ag layer. Hence, it is reasonable that NO

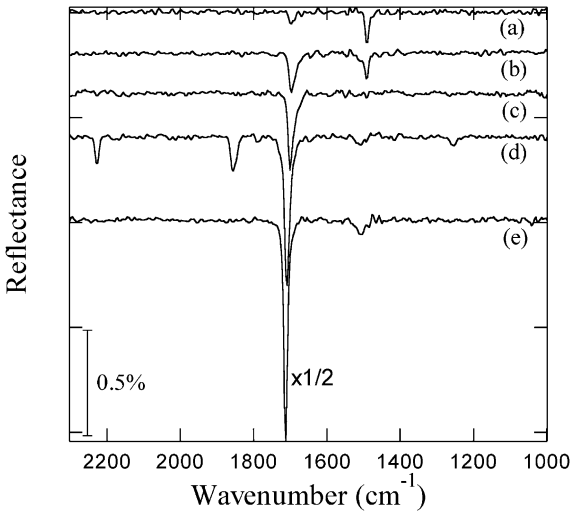

Fig. 1. RAIR spectra for NO adsorbed on a Ag(0.2 ML)/Pt(1 1 1) surface at 90 K with NO exposures of (a) 4 L, (b) 6 L, (c) 8 L, and (d) 100 L. (e) RAIR spectrum taken for pure Pt(1 1 1) after saturation of NO at 90 K with a reduced scale.

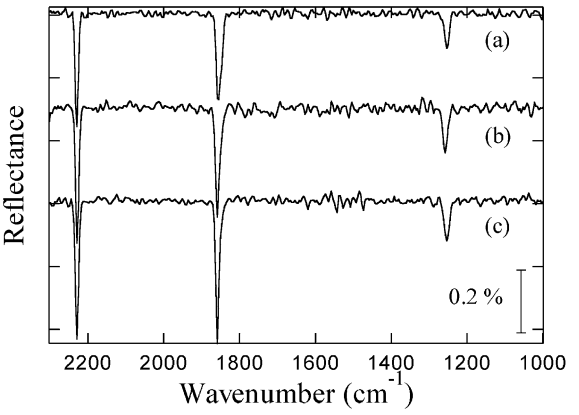

Fig. 2. RAIR spectra for NO adsorbed on a Ag(n ML)/Pt(1 1 1) surface at 90 K after exposure to 50 L; (a) 1 ML, (b) 2 ML, and (c) 7 ML.

adsorbs initially on the bare Pt(1 1 1) surface and subsequently sticks on the Ag-covered surface. Shown in Fig. 1(e) is the RAIR spectrum of NO at pure Pt(1 1 1) after saturation. Compared with this, it is noticed that the absorption band at around 1710 cm^{-1} is decreased in intensity and red-shifted by 5 cm^{-1} probably due to dipole interaction with NO on the Ag layer.

Fig. 2 shows RAIR spectra after an NO dosage of 50 L corresponding to saturation at Ag/Pt(1 1 1) surfaces where the Ag layer thickness was varied from 1 to 7 ML. No absorption bands corresponding to the NO species directly bound to Pt(1 1 1) appear in these spectra, and only the three bands corresponding to the ones adsorbed on the Ag layer are observed. According to a detailed study of the NO adsorption on Ag(1 1 1) [7,8], three absorption bands are observed at 1250, 2229, and 1855 cm^{-1} by RAIRS, the former two being assigned to N_2O and the latter assigned to $(NO)_2$. In the present work, the intensity of the bands at 1250 and 2229 cm^{-1} was found to change in a similar way depending on the dosage and temperature, therefore these two bands originate from the same species and can be assigned to the N–O and N–N stretching vibration of N_2O, respectively. It is noted that the band center and the width of the two bands do not change significantly with the Ag thickness. On the other hand, the width of the band at 1855 cm^{-1} is obviously broadened at a lower Ag-thickness: the full width at half maximum (FWHM) obtained from fits to a gaussian function is 16.3, 13.7, and 10.5 cm^{-1} for Ag thicknesses of 1, 3, and 7 ML, respectively. As shown later, the broadening of this band at an Ag thickness of 1 ML is due to the overlap of two bands centered at 1859 and 1848 cm^{-1}. As the Ag thickness increases, the intensity of the band at 1848 cm^{-1} is reduced resulting in narrowing of the FWHM together with slight shift of the band center to higher frequency. The integrated area of this band, however, is the same within our experimental accuracy because the peak height is more pronounced at an Ag thickness of 7 ML while the FWHM is reduced. It is worth noting that the width of the band at $\sim$1855 cm^{-1} is almost constant above Ag thicknesses of 3 ML.

The evidence for the presence of the two bands is given in the evolution of the RAIR spectrum as a function of time, which is displayed in Fig. 3. Fig. 3(a) demonstrates the RAIR spectra of NO adsorbed on Ag(10 ML)/Pt(1 1 1) taken 1–20 min after dosage of 50 L NO. The band intensity at 1859 cm^{-1} gradually decreases while those at 2229 and 1252 cm^{-1} substantially increases, suggesting conversion from the species corresponding to the

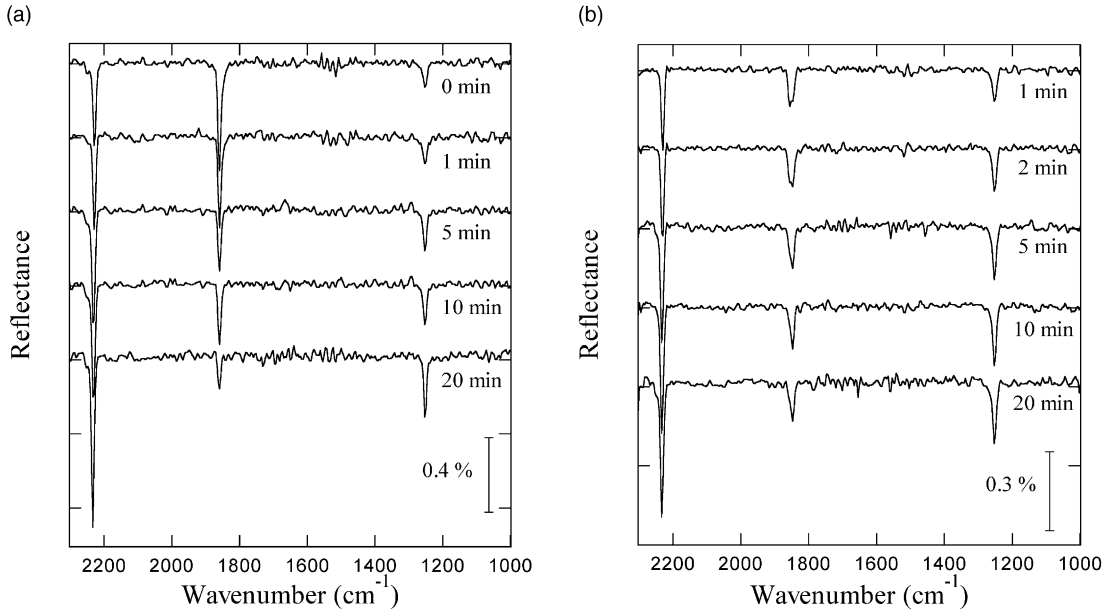

Fig. 3. Time evolution of RAIRS taken for NO adsorbed at (a) Ag(10 ML)/Pt(1 1 1) and (b) Ag(1 ML)/Pt(1 1 1) at 90 K after exposure of 50 L.

band at 1859 cm^{-1} to N_2O. According to the previous work by Brown et al. [7,8], the band at 1859 cm^{-1} is assigned to the symmetric stretching vibration of $(NO)_2$ which reacts into N_2O. Therefore, it can be concluded that the absorption band appearing at 1859 cm^{-1} on Ag(10 ML)/Pt(1 1 1) corresponds to $(NO)_2$. As discussed by Brown et al. [7,8], absence of the asymmetric stretching mode (gas-phase value: 1790 cm^{-1}) in RAIRS indicates that the dimer adsorbs with the N–N bond parallel to the surface. By fitting the data of the band intensity as a function of time to an exponential function $I_0 \exp(-kt)$ where t is the time and I_0 and k are fit parameters, the reaction rate k was estimated to be 3×10^{-3} s^{-1}. Compared with the reaction rate of 0.22 s^{-1} on Ag(1 1 1) at 90 K [8], the present value is two orders of magnitude smaller. This remarkable difference might be ascribed to the bimetallic electronic effect and/or geometric defects such as dislocations observed by STM [20]. In order to elucidate the mechanism, detailed measurements of the rate dependence on the temperature are necessary.

The time dependence of RAIRS taken for NO adsorbed on Ag(1 ML)/Pt(1 1 1) shown in Fig. 3(b) contrasts the results of Ag(10 ML)/Pt(1 1 1). The absorption band initially appearing at 1855 cm^{-1} is accompanied by a shoulder in the low-frequency side. As the time evolves, the band at 1855 cm^{-1} is attenuated and the band at 1848 cm^{-1} becomes more pronounced. At the same time, the intensity of the bands at 2229 and 1254 cm^{-1} is increased indicating a reaction to N_2O. Therefore, the species giving rise to the RAIRS band at 1855 cm^{-1} is assigned to the NO dimer. The reaction rate estimated from the decrease rate of the band intensity is about 3×10^{-3} s^{-1} which is the same as that on Ag(10 ML)/Pt(1 1 1). It should be emphasized that the species corresponding to the band at 1848 cm^{-1} does not undergo the reaction to N_2O but is rather stable.

Presence of the two bands at ~1855 cm^{-1} is further clearly demonstrated in the photon irradiation experiment. Shown in Fig. 4 are RAIR spectra for Ag(10 ML)/Pt(1 1 1) taken after photon irradiation at a wavelength of 193 nm. The laser fluence at the sample was about 1 mJ cm^{-2}. With increasing irradiation time, the intensity of the three bands at 2229, 1855, and 1254 cm^{-1} is decreased suggesting photo-induced desorption of

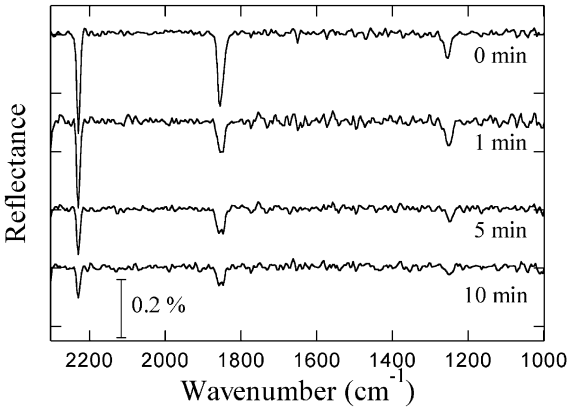

Fig. 4. RAIR spectra for NO adsorption of 50 L on Ag(1 ML)/Pt(1 1 1) at 90 K after photon irradiation ($h\lambda = 193$ nm) at laser fluence of 1 mJ cm^{-2} and a repetition rate of 10 Hz.

both species. Furthermore, the band at 1855 cm^{-1} splits into two bands centered at 1859 cm^{-1} and 1848 cm^{-1} as discussed above. From the decrease rate of the RAIRS band intensity, the desorption cross-section is estimated to be $\sim 10^{-18}$ cm^2.

The newly found species giving rise to the RAIRS band at 1848 cm^{-1} can be assigned to either monomer or dimer NO. At the present stage, we cannot decisively identify this species, hence we argue in the following the two possibilities. Note that the value of 1848 cm^{-1} is close to the stretching vibrational frequency of NO (1876 cm^{-1}) as well as the symmetric stretching vibration of $(NO)_2$ (1869 cm^{-1} [25,26]) in the gas phase.

A general feature observed for the bimetallic interface is the charge redistribution between the substrate and the overlayer [1,27]. In the case of Cu on several substrate surfaces, XPS studies showed a charge transfer takes place from the substrate to the Cu atoms [1,27]. Upon CO adsorption, the enhancement of the charge density in the Cu layer brought about an increase of the π back-donation leading to the increase of the CO adsorption energy [1,27]. The XPS data reported for the system of Ag/Pt(1 1 1) show a negative shift of the Ag 4d binding energy indicating a similar charge transfer from the Pt substrate to the Ag overlayer [28]. On the basis of the NO molecular orbital picture, the 2π orbital is responsible for the dimer formation as well as the bonding to the substrate [9,29]. From the analogy with the CO adsorption on thin Cu films, the π back-donation to adsorbed NO can be expected to be enhanced on Ag(1 ML)/Pt(1 1 1) compared to the adsorption on Ag(1 1 1). According to a theoretical calculation [9], the monomer state is less stable than the dimer state, and no monomer species has been experimentally observed [7,8] on the Ag(1 1 1) surface. On the Ag monolayer on Pt(1 1 1), however, the monomer state could be stabilized due to the increased π back-donation caused by the charge transfer between Ag and Pt. Since the 2π orbital of NO mainly responsible for bonding with the substrate has an antibonding character with respect to the N–O bond, such an enhancement of the π back-donation would cause a red-shift for the stretching vibration compared with the gas-phase value. Furthermore, hindering of the conversion into N_2O from this species as observed in Fig. 3(b) is readily understood.

On the other hand, the charge transfer into the Ag layer might modify the structure of the NO dimer. Provided that the NO dimer stands straight-up on the Ag monolayer on Pt(1 1 1) compared to the tilted geometry on Ag(1 1 1), the reaction into N_2O would be suppressed [7,8]. As observed in Fig. 4, the two species corresponding to 1848 and 1859 cm^{-1} are similarly depleted upon laser irradiation. This fact suggests that the two species are similar in nature and that the new species is a dimer. Since the NO 2π orbital is responsible for the dimer–substrate bonding, the enhancement of the π back-donation would cause a red-shift of the vibrational frequency compared with the value for the dimer on Ag(1 1 1).

We finally discuss the photodesorption mechanism. In the gas phase, the NO dimer absorbs light in the range 190–230 nm and subsequently undergoes dissociation producing electronically excited NO [30–32]. This direct photodissociation mechanism is discussed to be responsible for the NO desorption from condensed $(NO)_2$ films on Ag(1 1 1) [33] and MgF_2 [34] and $(NO)_2$ monolayer on LiF(0 0 1) [35]. In the monolayer regime on Ag(1 1 1), such a direct mechanism is also suggested to be operative at a wavelength shorter than 320 nm, although the NO dimer was assigned to the atop NO monomer in this paper [36]. The cross

section of the dimer photodissociation was 4.2×10^{-18} cm^2 on LiF(0 0 1) at 193 nm [35]. The cross section for the photodesorption from the dimer state was 3×10^{-18} cm^2 on Ag(1 1 1) [36]. Since the cross-section observed in the present study is comparable with the above values, the direct excitation of the NO dimer followed by dimer dissociation is the most probable process on Ag/Pt(1 1 1). It is noted that the temperature rise expected in this experiment (~8 K) might be close to the thermal desorption temperature. At the present stage, however, we rule out the possibility of the laser-induced thermal desorption because thermal excitation leads to N_2O production [7] which was not observed in our photoirradiation experiment as shown in Fig. 4. Note that we can not exclude the combined effect of thermal conversion of $(NO)_2$ into N_2O followed by photodesorption of N_2O. As for N_2O desorption, the direct excitation also seems to be responsible. The N_2O molecule formed on Ag(1 1 1) is reported to be inactive to photoexcitation at a wavelength of 340 nm. On the other hand, the N_2O molecule in the gas phase has an absorption band centered at 182 nm extending up to 230 nm causing photodissociation [37,38]. As we described in the introduction section, the dependence of the photodesorption on the thickness of the Ag film is a subject of importance, which will be presented in a forthcoming study.

4. Conclusion

The adsorption and photoreaction of NO on Ag films with thicknesses of 0.2–10 ML deposited on Pt(1 1 1) were investigated at 90 K by RAIRS. NO molecules were converted into $(NO)_2$ and N_2O on the Ag films. In addition to these two species, a new adsorption state giving rise to a RAIRS band at 1848 cm^{-1} was present at an Ag thickness of 1 ML. The NO dimer was found to react into N_2O with a reaction rate of 3×10^{-3} s^{-1} at an Ag thickness of 10 ML, while the newly found species did not undergo the reaction. Upon photon irradiation with a wavelength of 193 nm, both $(NO)_2$ and N_2O on Ag(1 ML)/Pt(1 1 1) were found to be depleted from the surface. The mechanism of direct molecular excitation followed by molecular dissociation was discussed.

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