

INTERACTION OF NO WITH CLEAN AND K-DOSED Rh(111) SURFACES

II. EELS and PES studies

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The interaction of NO with clean and potassium covered Rh(111) surfaces has been investigated by means of EELS (in the electronic range), UPS and XPS. The appearance of the O 2p signal at 6.0 eV in UPS indicates the dissociation of NO at low coverage on the clean surface at 300 K. At high exposures the adsorption is preferentially molecular. In the presence of a potassium adlayer the thermal stability of adsorbed NO depended on the potassium coverage. At low K coverage the potassium promotes the dissociation due to enhanced back-donation from the d-orbitals of Rh into the 2π orbital of NO. At monolayer K coverage, the UPS and XPS spectra suggest an appreciable stabilization of NO; the dissociation started at 400–422 K. Above 422 K, the appearance of new photoemission signals at 4.0, 9.8 and 11.7 eV in UPS, and at 403.8 and 533.7 eV in XPS suggest the formation of NO₂ species stabilized by potassium. This surface complex decomposes on Rh(111) at around 664 K.

1. Introduction

Earlier we investigated the adsorption and desorption of NO on a K-dosed Rh(111) surface by Auger electron, work function and thermal desorption measurements [1]. In the present work, electron energy loss spectroscopy (EELS) (in the electronic range), ultraviolet (UPS) and X-ray photoelectron spectroscopy (XPS) are used to obtain a deeper insight into the nature of the interaction.

Electronic EELS has already been successfully applied in our laboratory in the study of the adsorption and reactions of several N-containing molecules, such as HNCO [2–5], HCN [6] and C₂N₂ [7–9].

The EEL spectrum of adsorbed NO has so far been taken for example on the Ni(100) surface at 300 K [10], on Al [11] and on W [12], where molecularly and dissociatively adsorbed NO were detected.

UPS has been used more extensively in the study of NO adsorption on different metal surfaces, for example on Ru [13], Pt [14], Ir [15] and Pd [16], to mention only works performed on the Pt metals, which are of most relevance to the

present study. The UP spectrum of NO adsorbed on a Rh single crystal was investigated by Baird et al. [17]. They observed that NO chemisorbs dissociatively at low coverages, followed by its non-dissociative chemisorption at higher exposures at 300 K.

2. Experimental

Sample preparation and experimental arrangement are given in a former publication [1]. Potassium was deposited on Rh(111) at room temperature by resistively heating a getter wire source (SAES getter) located 2 cm from the sample. The K coverage was calibrated using AES and TPD yield, and was described elsewhere [18]. EEL spectra were recorded by both cylindrical mirror (PHI) and retarding field (VG) analysers. The energy of primary electron beam was 70.0 eV, while its current-density was around 1 $\mu\text{A}/\text{cm}^2$.

UP spectra were taken using the HeII resonance line. The angles between the surface normal and UV lamp and between the surface normal and the analyzer were 75° and 16°, respectively. Difference spectra are reported for experiments with

and without NO adsorption at a given θ_K . The photoelectrons were excited by Al K α radiation (1486.7 eV) in the XPS regime and they were recorded by a hemispherical analyzer (Leybold-Heraeus LHS-10).

3. Results

3.1. EELS studies

3.1.1. Clean surface

The EEL spectrum of the clean Rh(111) surface has been studied by a number of workers [19–22]. As it has been pointed out the positions of losses are influenced by preparation, orientation and cleanness of the samples as well as by the detec-

tion mode of scattered electrons [4]. The characteristic Rh losses in the present case appeared at 3.0, 5.2–6.7 and 21.0 eV (fig. 1) in accord with our previous findings [4,5,8,9].

On exposure of this surface to NO at 300 K, a new loss developed at 6.4 eV from the broad loss feature of Rh between 5.2 and 6.7 eV. The intensity of the 6.4 eV loss increased with the NO exposure and in the meantime other losses were produced at 10.0 and 15.0 eV. The positions of these latter losses shifted slightly to higher energy with increase of the exposure.

When the NO-saturated surface was gradually heated to higher temperatures, the 6.4, 10.0 and 15.0 eV losses disappeared above 432 K (fig. 1B). These temperatures correspond well to the T_p values for NO desorption [1].

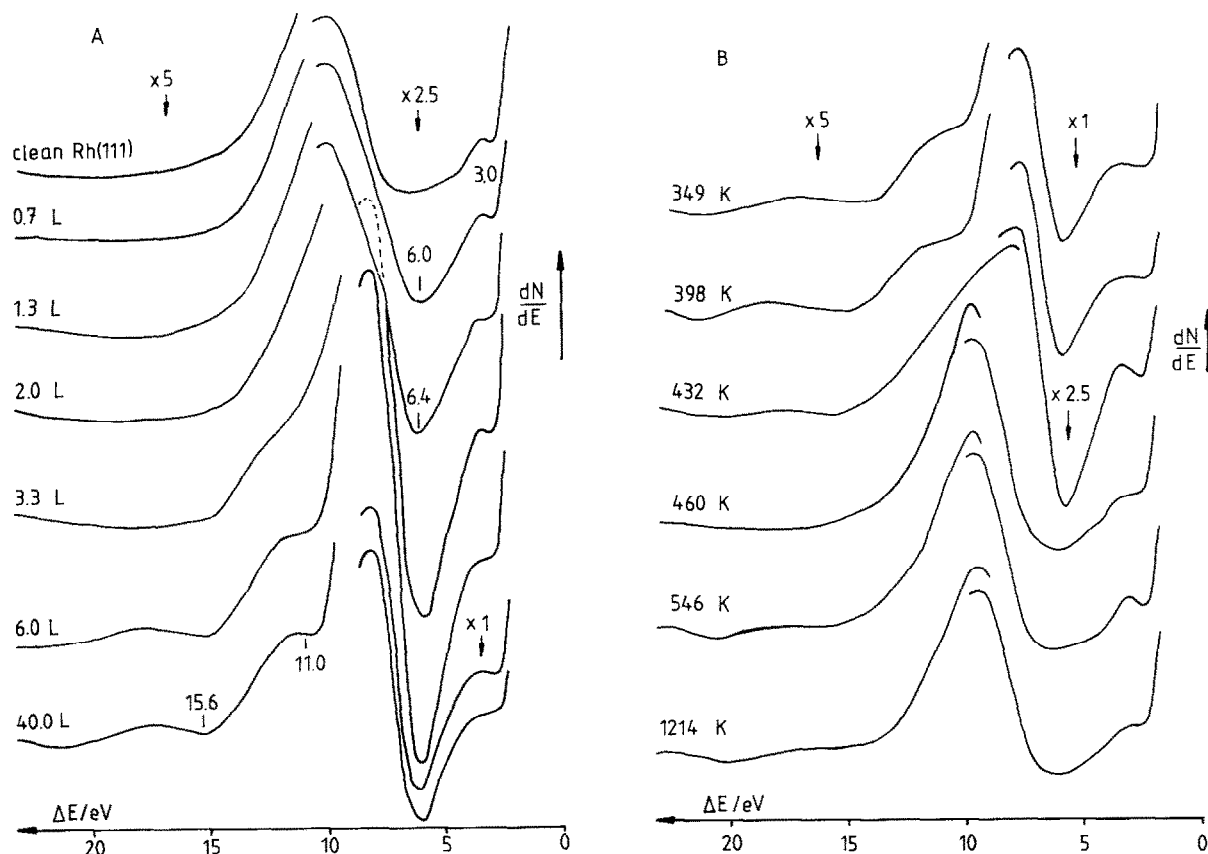


Fig. 1. EEL spectra of Rh(111) following NO adsorption at 300 K (A) and after heating the NO saturated surface to higher temperatures (B).

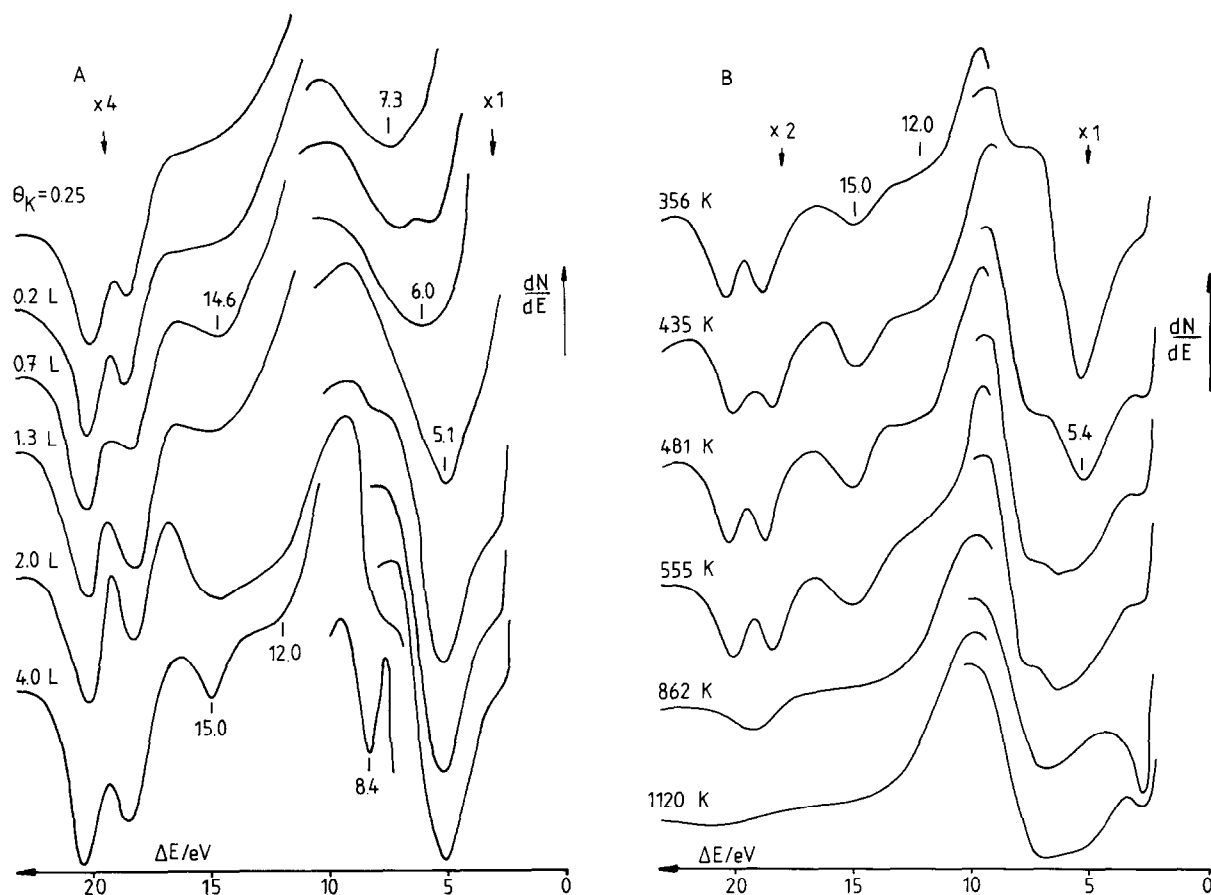


Fig. 2. EEL spectra of potassium-dosed Rh(111) ($\theta_K = 0.25$) as a function of NO-exposure at 300 K (A) and after heating the NO-saturated layer to higher temperatures (B).

3.1.2. Potassium-dosed surface

The deposition of K at 300 K produced a sharp loss at 7.3 eV from the broad loss feature of Rh between 6.7 and 5.2 eV (fig. 2). EEL peaks appeared at 18.5 and 20.0 eV following K adsorption, too. Similarly as in our previous work [18], at higher K coverage a new loss attributable to K adsorbed in metallic-like form appeared at 2.3 eV.

The adsorption of NO on K-covered Rh(111) at $\theta_K = 0.25$ at 300 K produced losses near the same energies (6.0 and 14.6–15.0 eV) as for the clean surface (fig. 2A). A new feature developed at 8.4 eV on the K-dosed sample. With increase of the exposure, the 6.0 eV loss was shifted to 5.1 eV and another peak appeared near 12.0 eV. These losses disappeared at higher temperatures than on the K-free surface. The temperatures were ~ 470

K for the 5.1 eV, 600 K for the 12.0 eV and 780 K for the 15.0 eV losses (fig. 2B).

The intensity changes of the 5.1–6.4 eV losses under various conditions are depicted in fig. 3.

3.2. UPS studies

3.2.1. Clean surface

The adsorption of NO on the clean surface at 300 K attenuated the intensity of the d-band of Rh near the Fermi level and at low exposure (0.2 L) produced a strong photoemission peak at around 6 eV in the He II difference spectrum (fig. 4A). At the same time, very weak emissions were also observed at 8.9 and 14.8 eV. With increase of the exposure, the intensity of the emission at 6.0 eV remained constant, but the other two emissions

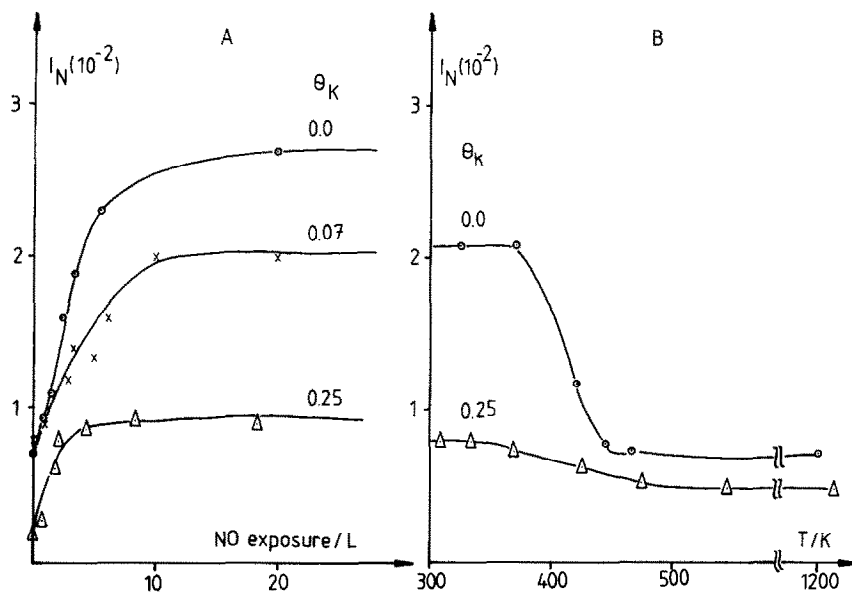


Fig. 3. The intensity changes of 6.0 eV loss characteristic for molecularly adsorbed NO, as a function of NO-exposure (A) and temperature of the adsorbed layer (B) on potassium-free and potassium-covered Rh(111) surfaces. In this case the NO exposure was 20 L.

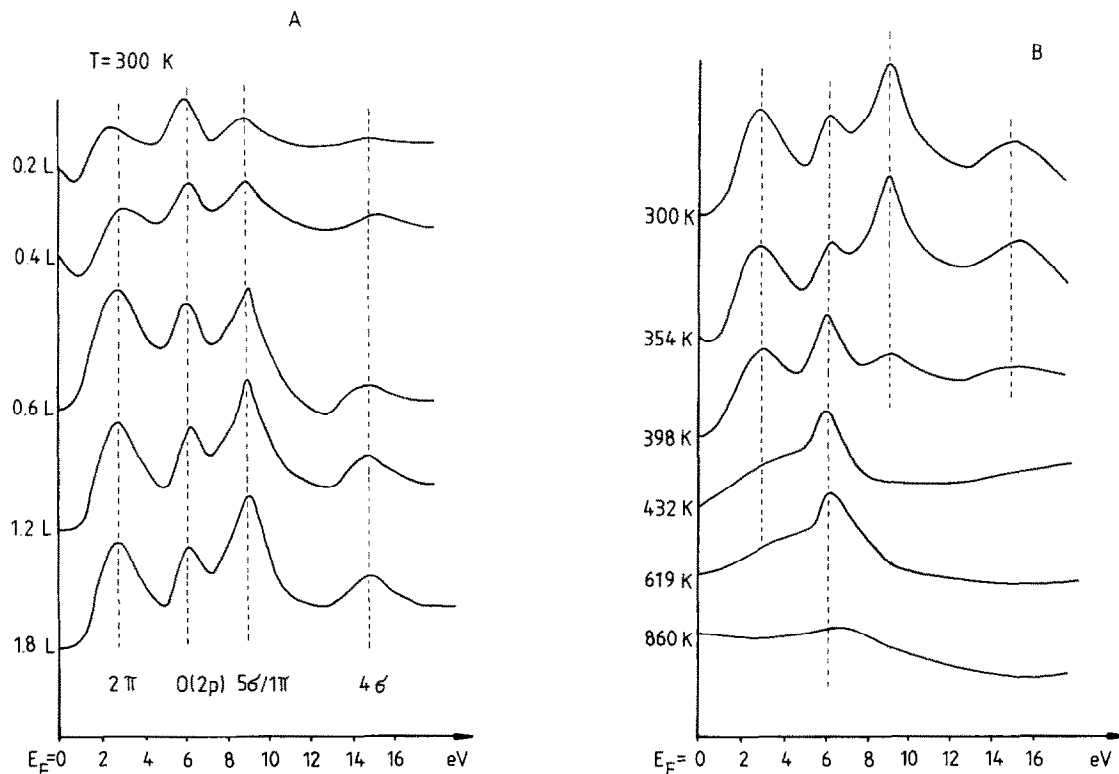


Fig. 4. HeII photoelectron difference spectra following NO adsorption on Rh(111) at 300 K (A) and after gradually heating the saturated layer to different temperatures (B).

became more intense. A significant increase was also observed in the region of the d-band at around 2.9–3.0 eV. When the adsorption of NO was carried out at 90 K, the 6.0 eV signal was completely missing.

When the NO-saturated surface was heated, the intensities of the peaks at 8.9 and 14.8 eV decreased above 354 K and these peaks disappeared at 400–432 K together with that at 2.8–3.0 eV. The peak at 6.0 eV was more stable; it was detectable up to 860 K (fig. 4B).

3.2.2. Potassium-dosed surface

Deposition of potassium on Rh(111) decreased and broadened the emission of the d-band of Rh. In the presence of potassium the K 3p level appeared at 17.9–17.5 eV in the He II spectrum.

The adsorption of NO was first investigated at low K coverage, $\theta_K \approx 0.1$, where the largest work function change was observed [18].

At low NO exposure (0.2 L), only one new photoemission signal was observed, at 5.8–6.0 eV. In contrast with the clean surface, the peaks at 8.9

and 14.5–15.0 eV appeared only at 0.4 L NO exposure (fig. 5A), and the K 3p level at around 17.9 eV intensified and moved to somewhat lower binding energy. Above an NO exposure of 0.4 L, the same change was observed near the Fermi level at 2.8–3.0 eV as on the clean Rh(111) surface. We note that the UP spectrum of adsorbed NO taken at 90 K agreed well with that registered for the K free surface at the same temperature: in this case the 6 eV peak is missing.

When the surface covered by NO at 300 K was heated to higher temperatures, the first change was observed above 369 K. The emissions at 2.8, 8.9 and 14.5 eV decreased and the level at 5.5–6.0 eV increased significantly (fig. 5B). Both peaks at 8.9 and 14.5 eV vanished between 398 and 422 K, while the 6.0 eV peak did so only at 900 K.

The adsorption of NO on Rh(111) at high K coverage, $\theta_K = 0.33$, produced emissions at 2.8, 8.9 and 14.5 eV in the He II difference spectrum, even at very low NO exposure (fig. 6A). The K 3p level at 17.5 eV strongly intensified and shifted to 17.0 eV. The most interesting feature is that, in

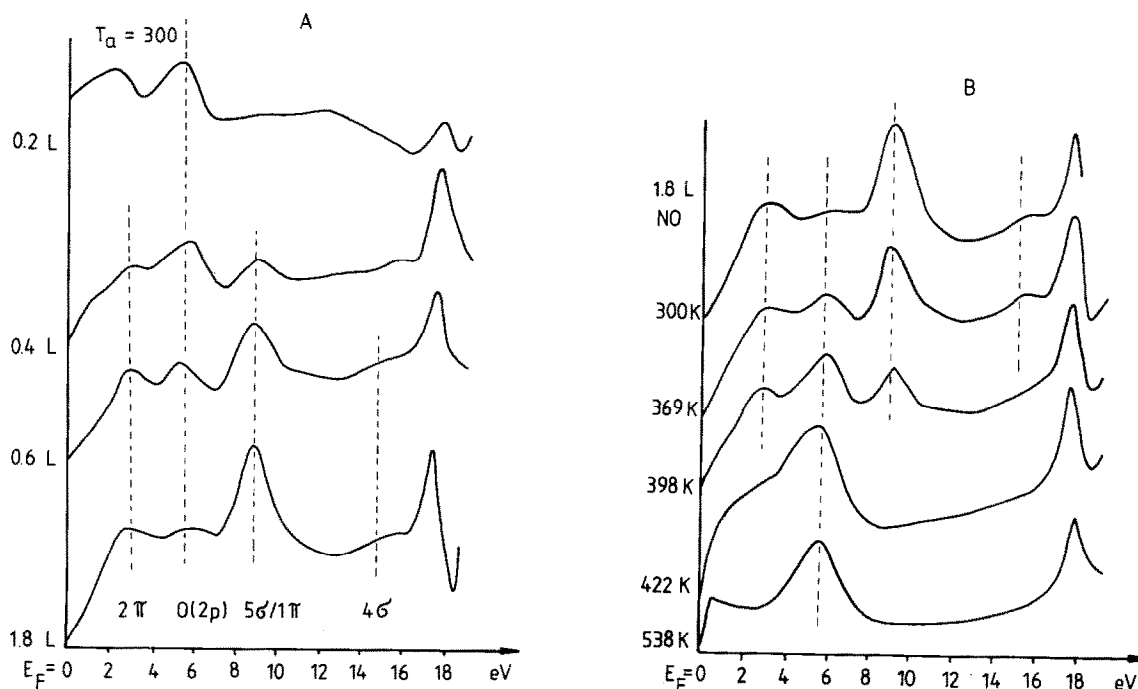


Fig. 5. He II photoelectron difference spectra following NO adsorption on K-promoted Rh(111) at 300 K (A) and after heating the adsorbed layer to different temperatures (B). $\theta_K = 0.1$.

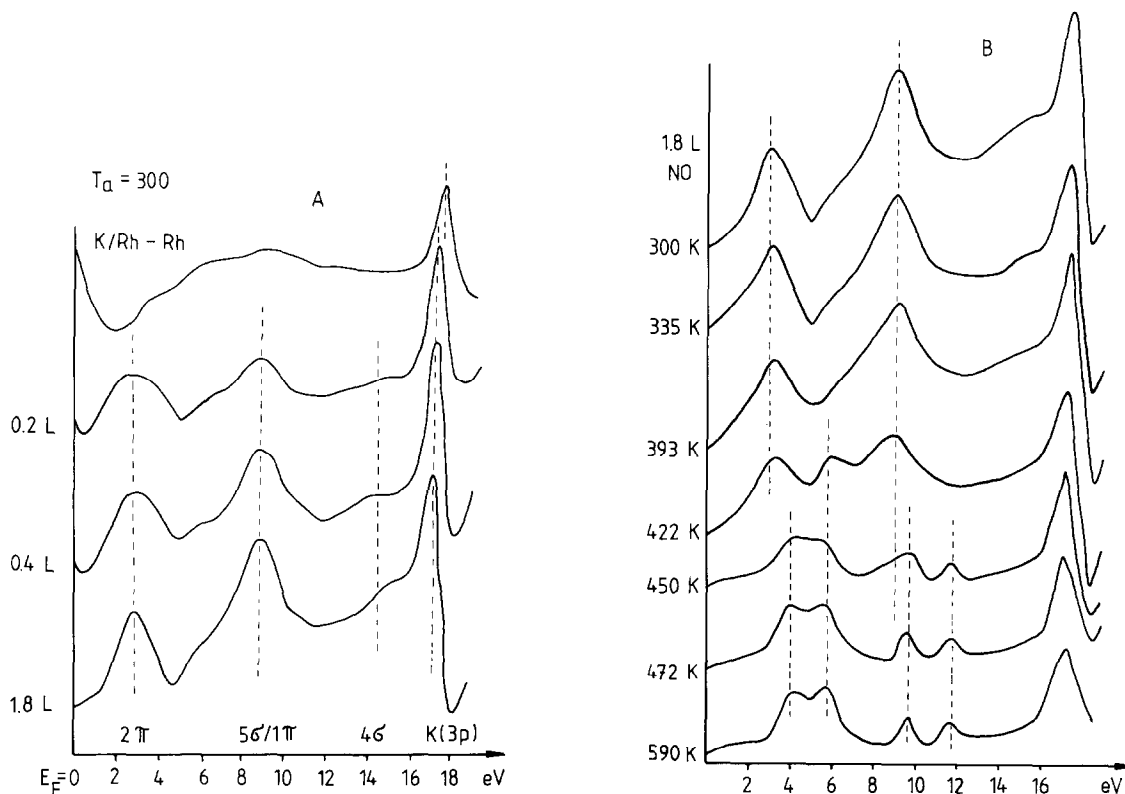


Fig. 6. HeII photoelectron difference spectra following NO adsorption on K-promoted Rh(111) at 300 K (A) and after heating the adsorbed layer to different temperatures (B) $\theta_K = 0.33$. The difference spectrum of K-dosed and K-free Rh(111) are also shown.

contrast with the clean or K-dosed surface at $\theta_K \approx 0.1$, the photoemission peak at 6.0 eV was not or hardly detectable in this case either at 100 or 300 K. Upon heating, the intensities of the observed orbitals decreased only above 393 K, and the peaks disappeared at 470 K (fig. 6B). In parallel with these changes, new features were observed at 4.0, 6.0 eV (422 K) and 9.8 and 11.7 eV (454 K). The latter two peaks disappeared at 643 K, and the peak at 4.0 eV at slightly higher temperature. The same conclusions can be drawn from an analysis of the normal UP spectra. The emission at 6.0 eV exhibited a maximum at 643 K and vanished only above 900 K.

3.3. XPS measurements

3.3.1. Clean surface

Adsorption of NO on the clean surface at 90 K

produced the O 1s peak at 531.4 eV and the N 1s peak at 400.3 eV (with broadening on the higher-energy side), which are characteristic of the adsorbed NO molecule [17]. When the saturated layer was heated to 374 K, the position of the O 1s peak moved to somewhat lower binding energy (~ 530.5 eV), indicating that the NO molecules dissociated. The occurrence of NO dissociation was also exhibited in the N 1s region of the spectrum: a low-intensity peak appeared at 397.5 eV, which is due to the adsorbed N atom [17].

3.3.2. Potassium-dosed surface

The peak positions for molecularly adsorbed NO at 300 K altered only slightly in the presence of K: peaks at 531.3 eV for O 1s and 400.4 eV for N 1s were observed at $\theta_K \approx 0.33$ (fig. 7). When the surface exposed to 18 L NO was heated to 470 K, not only the weak peak characteristic of atomic N

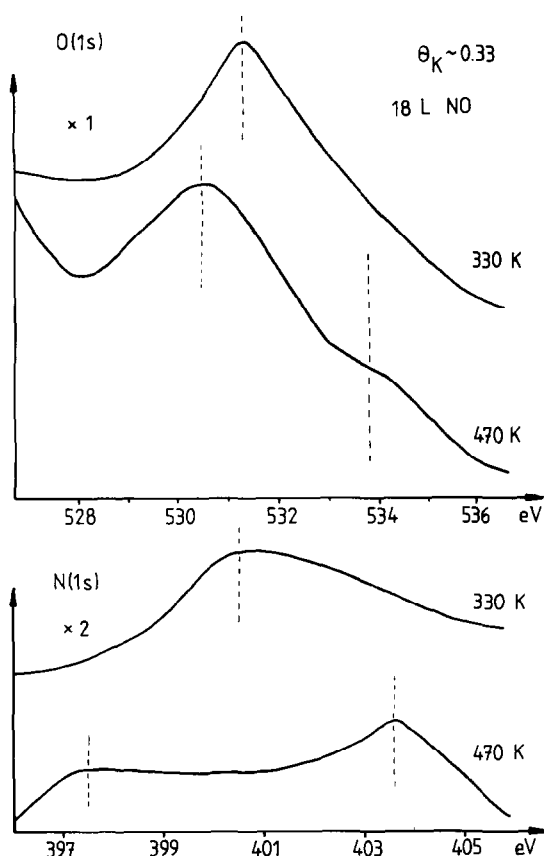


Fig. 7. X-ray photoemission spectra of NO adsorbed on potassium covered Rh(111) ($\theta_K \approx 0.33$). The surface was exposed at 300 K and then heated up to higher temperatures.

at 397.5 eV and the strong signal of atomic O at 530.5 eV appeared, but also a new peak at 403.6 eV and a shoulder at 533.8 eV, suggesting the formation of new surface species on the K-dosed surface. These features disappeared above 600 K. When the sample was exposed to NO at 470 K, the intensities of these new peaks were greatly enhanced.

4. Discussion

4.1. Clean surface

The adsorption of NO on a clean Rh surface has been investigated by a number of techniques, but no ELS and UPS measurements have been

performed on the Rh(111) surface. Previous work [1,17,23–32] demonstrated that the initial adsorption of NO on the Rh single crystal surface is dissociative at 300 K. At higher NO coverage the adsorption is molecular.

Two molecular states of NO have been identified by TDS, XPS and HREELS, which exhibit different chemical reactivities [26,27,32]. These states were assigned to the bent $(\text{Rh-NO})^-$ and to the linear $(\text{Rh-NO})^+$ species. The negatively charged species should couple more strongly with the metal electrons, weaken the N–O bond and increase the tendency to dissociation [27].

Following NO adsorption at 90 K, new UPS signals were produced at 2.8–3.0, 8.9 and 14.5 eV below the Fermi level. These emissions are characteristic of molecularly adsorbed NO [13–17] and clearly support the conclusion [1] that NO adsorbs molecularly on clean Rh(111) at around 100 K. The NO-induced emission can be attributed to the $2\pi^*$, $1\pi/5\sigma$ and 4σ levels, respectively.

In the EEL spectrum three losses were registered at 6.0–6.4, 10.0–11.0 and 15.0–15.6 eV, at both 100 and 300 K. With regard to the orbitals observed in the He II photoemission spectra, the loss at 6.0 eV is tentatively assigned to an intramolecular transition from the occupied $2\pi^*$ orbital of NO to an unoccupied state 3 eV above the Fermi level. The 10.0–11.0 and 15.0–15.6 eV losses are attributed to the electron transitions from the $1\pi/5\sigma$ and 4σ orbitals to the Fermi level, respectively. The positions of these losses differ somewhat from those observed on other metals (see table 1). A possible reason for this difference is that these metals are more reactive than Rh towards NO and as a result the NO underwent a more significant dissociation.

When the adsorption was performed at 300 K, an additional UPS signal was observed at 6.0 eV, which is associated with the 2p level of adsorbed oxygen. This suggests the occurrence of NO dissociation. The intensity of this signal observed at low NO exposure remained constant with increase of the surface concentration of adsorbed NO, but increased with the sample temperature. The maximum extent of dissociation was attained at around 432 K, which coincides with the peak temperature of the desorption of β_2 -NO. In harmony with this,

Table 1
Electron energy loss characteristics for different metal surfaces covered with NO

Substrate	T_{ad} (K)	Losses (eV)	Origin of losses	Ref.
Ni(100)	300	4.8	NO(ad)	[10]
		10.2		
		12.0		
		15.2		
Al(100)	300	5.8	Al-N + Al-O adlayer	[11]
		12.4		
		20.0		
W(110)	300	7.0	Dissociated NO	[12]
		12.0		
	80	6.6	NO(ad)	
		14.0		
Rh(111)	300	6.0–6.4	NO(ad)	[This work]
		10.0–11.0		
		15.0–15.6		
	100	6.0–6.2	NO(ad)	
		10.0–11.0		
		15.0–15.6		

XPS measurements revealed binding energies at 530.5 eV (O 1s) and 397.4 eV (N 1s) at 447 K due only to atomic oxygen and nitrogen, respectively. The results obtained suggest that the dissociation of NO is limited on Rh(111) at 300 K, and very probably proceeds only on certain surface defect sites. The calculations of DeLouise and Vinograd [27], based on XPS measurements, showed that only 3% of the saturated layer dissociates at 300 K. It should also be taken into account that the dissociation of NO in the saturated layer is hampered as it requires free adsorption centers in the vicinity of molecularly adsorbed NO.

In the EEL spectrum, there was no indication of dissociation of NO. This is not surprising, as neither adsorbed O nor adsorbed N gave losses on the carefully cleaned Rh(111) surface [33]. An intense loss feature was observed at 9.5 eV when the surface contained boron impurities this loss was attributed to oxygen adsorbed on boron [33].

4.2. Potassium-dosed surface

Our previous AES, TDS and work function measurements on the NO + K/Rh(111) system showed that K adatoms increase the uptake of NO, promote the dissociation of NO, and induce secondary reactions; at the same time, the K itself is also stabilized in the coadsorbed layer [1]. Some of these features have been demonstrated by time-resolved EELS on the Rh(100) surface [34]. The above characteristics agreed well with those observed by other authors for K-dosed Ag [35–37] and Pt(111) [38,39] surfaces. The present UPS and EELS results provide more details on the interaction of NO with K-promoted Rh(111).

The photoemission peaks and EELS losses for NO adsorbed on a K-covered surface at 90 K appeared practically at the same energies as on the clean surface. There was no indication of dissociation of NO at this temperature at any K coverage. However, at higher temperatures the thermal stability of the adsorbed NO depended on the K coverage, i.e. on whether it was in the ionic state ($\theta_K \approx 0.15$) or the metallic form ($\theta_K \approx 0.3$).

4.2.1. Low potassium coverage ($\theta_K = 0.1$)

When the NO was adsorbed at 300 K at low exposures, the intensity of the oxygen signal (6.0 eV) relative to that of the NO signal at 8.9 eV was higher than observed for the clean surface. This indicates that K promotes the dissociation of NO at this K coverage. This effect of K was exhibited at higher temperatures, too. The analysis of our previous TPD measurements [1] revealed that 67% of the adsorbed NO underwent dissociation during heating of the saturated layer on the clean surface, while almost 93% of the adsorbed NO dissociated on K-promoted Rh(111) at $\theta_K = 0.1$.

It is an important observation that the adsorption of NO on a K-dosed surface ($\theta_K = 0.08$) caused an increase of 1.3 eV in the work function, which means that the adsorbed NO has a negative outward dipole moment. The effect of K can be interpreted in terms of the charge-transfer model [40], e.g. the presence of K increases the extent of back-donation from the d orbitals of the Rh into the $2\pi^*$ orbital of the NO ligands.

The enhanced charge transfer between NO and

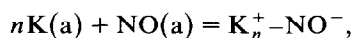
the K/Rh surface results in the formation of partially negatively charged NO species, and leads to a considerable weakening of the N–O bond and to an increased probability of its dissociation.

From an analysis of the UPS spectra it appears that the above charge-transfer process does not lead to an appreciable stabilization of NO adsorbed at low K coverage. This is in accord with the TDS results [1], where less than a 5 kJ/mol increase was measured in the activation energy of NO desorption at this K coverage. This is in contrast with the behavior of CO adsorbed on K-dosed metal surfaces: even at low K coverage (at $\theta_K = 0.1$), the binding energy of the adsorbed CO increased by at least 20 kJ/mol [40–42].

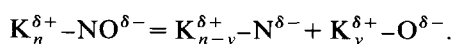
4.2.2. High potassium coverage ($\theta_K \approx 0.33$)

In this case a completely different picture was observed: dissociation of NO was not found at 300 K at any coverage. This process occurred only at the higher temperatures of 400–422 K. The emission of molecularly adsorbed NO attenuated from 422 K and disappeared at ~ 472 K. This temperature is about 30 K higher than that obtained for the clean surface (fig. 6B). The intensity changes of the loss at 5.1–6.0 eV in the EELS suggested a similar picture (fig. 3). We note here that an increase of 20 K in the temperature of α_1 -NO dissociation was earlier observed on a K-precovered Rh(100) surface [34].

The results of work function measurements exclude the possibility that a more extended electronic interaction through Rh (compared with the previous two cases, $\theta_K = 0.0$ and $\theta_K \approx 0.1$) is responsible for this feature. It is more likely that a direct interaction occurs between adsorbed NO and metallic K, resulting in the formation of a K–NO surface complex:



which leads to the stabilization of NO adsorbed on the Rh(111) surface. When the coadsorbed layer is heated, most of the partially negatively charged NO decomposes to adsorbed N and O:



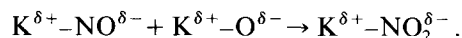
As both species are stabilized on the surface (the

T_p values for the associative desorption of N and O increase by at least 20 and 40 K, respectively, compared with the values determined for the clean Rh(111) surface [40,43] we can conclude that the linkages between the constituents of the NO molecule and the K metal do not cease after NO dissociation.

An interesting feature of the EEL spectra of the coadsorbed layer is the appearance of a loss feature at 8.4 eV (fig. 2A). We assume that this loss is the result of the same electron transition as suggested for the 10.0 eV loss in the case of the clean surface. The possible reason of this shift is the different final state of the K-dosed surface. Another characteristic is that the loss peak around 15.0 eV exhibited a high thermal stability; it was discernable up to 780 K, where only the dissociation products of NO were present on the surface. Accordingly, this loss cannot be attributed to adsorbed NO species. We assume that this loss is associated with $\text{K}^{\delta+} - \text{O}^{\delta-}$ species formed in the dissociation of the $\text{K}^{\delta+} - \text{NO}^{\delta-}$ complex. This conclusion seems to be supported by the observation that the adsorption of oxygen on K-dosed Rh(111) at this K coverage also produced a loss peak at this energy, which disappeared only above 800 K [43]. A very stable loss feature also developed at 15.0 eV when the CO_2 decomposed on K/Rh(111) surface above 300 K [18]. As regards the origin of the other loss at 12.0 eV obtained for this K-coverage, we mention that the adsorption of CO on K-dosed metal also produced a loss at the same energy [42]. Therefore, we tentatively attribute this feature to CO adsorbed from the background and stabilized by potassium.

An interesting feature of the interaction of NO with a K + Rh surface at this coverage is that the disappearance of the NO signals at around 470 K is accompanied by the appearance of new UPS emissions at 4.0, 9.8 and 11.7 eV. The fact that no or only very limited desorption occurred between 400 and 500 K strongly suggests that a fraction of the stabilized NO is transformed into a new surface compound above 422 K. The positions of these emissions agree well with those of NO_2^- species [39,44] and can be assigned to the $6a_1$, $1a_2$; $1b$ and $5a$ orbitals [45]. This suggests that NO reacts with adsorbed oxygen formed in the dissociation to

give partially negatively charged NO₂:



As NO₂ is a rather unstable species on Pt metals (it decomposes below 285 K on Pt(111) and Ru(001) surfaces [46–49]), it is probably being associated and stabilized by K. Spectral features of the formation of NO₂⁻ species were not observed on K-dosed Rh(100) [34], Ag(111) [35–37] and Pt(111) [38], but this process was clearly established on other Pt(111) samples [39].

The formation of NO₂ is supported by our XPS measurements, too. When the coadsorbed layer was heated to around 470 K, a shoulder appeared at 533.8 eV in the O 1s spectrum, while an intense N 1s peak was noted at 403.6 eV. An XPS study of KNO₂ adsorption on Fe and Pt surfaces [50] yielded similar binding energies: 404.5 eV for N 1s and 533.3 eV for O 1s. The temperature for which the photoemission peaks disappear due to NO₂ on K-promoted Rh(111) is around 664 K. This temperature approximates well to the peak of the high-temperature desorption of NO ($T_p \approx 700$ K) from K-dosed Rh(111) [1], which we attribute to the decomposition of the surface compound “K–NO₂” on Rh(111). We note that we could not detect a desorption signal of mass 46 (NO₂), and that the decomposition temperature of KNO₂ on Pt or Fe substrates was found to be near 600 K [50].

5. Conclusions

(1) NO chemisorbs dissociatively at low coverages followed by non-dissociative chemisorption at higher exposure on clean Rh(111) at 300 K.

(2) The preadsorbed potassium on Rh(111) increased the extent of NO dissociation at low potassium coverage ($\theta_K \approx 0.1$) at 300 K.

(3) At monolayer potassium coverage, NO is stabilized and dissociates only at 400–422 K.

(4) At around 422 K, a fraction of NO reacts with O formed in the dissociation process yielding NO₂⁻ species, which is strongly stabilized by potassium.

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