Adsorption and decomposition of NO on K-deposited Pd(1 1 1)

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Received 9 April 2003; accepted for publication 5 August 2003

Abstract

The adsorption and decomposition of NO on a K-deposited Pd(1 1 1) surface were investigated using X-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy, and temperature-programmed desorption. For the K-deposited Pd(1 1 1) surface, two different NO adsorption sites were observed in addition to the Pd site. On the clean Pd(1 1 1) surface, the adsorption of NO was purely molecular and reversible, but on the K-deposited surface, the adsorbed NO decomposed at two different temperatures, 530 and 610 K. These results indicate that the NO adsorption and decomposition sites were newly created by the deposition of K onto the Pd(1 1 1) surface.

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Keywords: X-ray photoelectron spectroscopy; Infrared absorption spectroscopy; Thermal desorption spectroscopy; Alkali metals; Palladium; Nitrogen oxides; Single crystal surfaces

1. Introduction

The direct decomposition of NO to N₂ and O₂ over solid catalysts is a promising method for removing this pollutant from exhaust streams. Transition metal surfaces are known to effectively adsorb and dissociate NO [1]. The direct decomposition of NO over supported noble metal catalysts such as Rh, Pt, and Pd has been extensively studied [2–4]. In addition, the influence of the surface structure and the presence of different metals on NO decomposition over noble-metal single-crystal surfaces have been examined using surface science techniques [5]. The addition of alkali to metal surfaces is known to change the electronic properties and consequently promote the catalytic activity [6]. Fundamental investigations of the effects of alkali metals on NO decomposition over noble-metal single-crystal surfaces have been performed [7–10].

For example, the influence of deposited potassium on the adsorption and dissociation of NO over Pt(1 1 1) has been studied by means of X-ray photoelectron spectroscopy (XPS) [7]. The dissociation of NO occurs on K-deposited Pt(1 1 1) surfaces, owing to an increase in the backdonation of surface electrons into the 2π molecular orbital of NO. In addition to XPS, temperature-programmed desorption (TPD) has also been used...
to examine the decomposition of NO adsorbed on K-deposited Pt(111) surfaces [8]. The desorption of N₂ and N₂O has also been observed for K/Pt(111). With increasing K coverage, the amount of N₂ and N₂O desorption increases, whereas the amount of NO desorption steadily decreases. The effect of Na on the decomposition of NO over Ag(110) [9] and Ag(111) [10] has been investigated by TPD. NO dissociation occurs on both Na-deposited Ag surfaces, as indicated by the detection of N₂ desorption.

Thus, it has been found that NO dissociation sites are created by the deposition of alkali metals onto Pt or Ag surfaces. However, the details of the relationship between the adsorption and decomposition sites of NO are not clear. To elucidate the relationship between the NO adsorption and decomposition sites on K/Pd(111), we examined the effect of K deposition on the reactivity of NO using XPS, infrared reflection absorption spectroscopy (IRAS), and TPD.

2. Experimental

The XPS experiments were carried out in an ultrahigh vacuum (UHV) apparatus composed of two chambers: a surface analysis chamber (<1 x 10⁻¹⁰ Torr) and a preparation chamber (<2 x 10⁻⁹ Torr). The analysis chamber was equipped with a photoelectron analyzer for XPS, an ion gun for Ar⁺ sputtering, and a leak valve for the NO exposure. A SAES getter source for the deposition of potassium onto the Pd surface was situated in the preparation chamber. XP spectra were measured with Mg Kα radiation. The IRAS and TPD experiments were performed in an UHV apparatus described in detail elsewhere [11]. The IRA spectra were recorded with a resolution of 4 cm⁻¹ by 100 scans (30 s).

The Pd(111) single-crystal disc (10-mm diameter, 1-mm thickness, 99.999% purity) was polished on only one side. The crystal orientation was accurate to within 1 degree, and the surface roughness was <0.03 µm. The Pd(111) surface was cleaned by cycles of Ar⁺ sputtering and annealing in oxygen at 1000 K and then by annealing at 1200 K in a vacuum. The surface cleanliness of the sample was verified by XPS or Auger electron spectroscopy (AES). However, because the AES peak of C(KLL) overlapped with the Pd(MNN) peak, the absence of carbon impurities was confirmed by the lack of CO and CO₂ thermal desorption following the saturated adsorption of oxygen at room temperature.

Potassium was deposited onto the clean Pd(111) surface at a substrate temperature of 300–320 K using the SAES getter alkali dispenser. The K-deposition rate was typically 0.03 monolayer/min at a passing current of 7.0 A. A coverage (θ) of 1 corresponded to the number of surface Pd atoms (1.53 x 10¹⁵ atoms/cm²). The coverage was estimated by XPS on the basis of the CO-buildup curve at room temperature; the CO saturation coverage on the Pd(111) surface was considered to be 0.5 [12]. The K and N coverages were determined from the peak area ratios of K 2p₃/₂/Pd 3d₅/₂ and N 1s/Pd 3d₅/₂, respectively, using the peak area ratio of C 1s/Pd 3d₅/₂ obtained from the CO saturation coverage and the sensitivity factors for C 1s, K 2p₃/₂, and N 1s.

The NO adsorption experiments were carried out using ¹⁵NO (99.9% pure) at 5 x 10⁻⁹–5 x 10⁻⁸ Torr of NO pressure and a sample temperature of 320 K. The ¹⁵NO gas was used to distinguish N₂ from CO desorption peaks as well as N₂O from CO₂ desorption peaks during TPD. The TPD experiments were performed with 1.0 K/s heating rate.

3. Results and discussion

3.1. NO adsorption

The K-deposited Pd(111) surfaces after NO exposure were analyzed by XPS. Fig. 1 shows the N 1s spectra for K/Pd(111) surfaces at various initial K coverages measured after NO exposure at 320 K and 3.8 L. The peak at 400.6 eV for the clean Pd(111) surface was assigned to molecularly adsorbed NO [13]. At 320 K, the clean Pd(111) surface became saturated at around 1.5 L of NO exposure, and the estimated NO saturation coverage was 0.25, which is in good agreement with the value reported for Pd(111) at 300 K [14].
Potassium deposition on the Pd(1 1 1) surface shifted the N 1s peak toward a lower binding energy: at $\Theta_K = 0.10$, the binding energy was 400.5 eV, and with increasing K coverage, the binding energy decreased even farther, reaching 400.1 eV at $\Theta_K = 0.21$. Above $\Theta_K = 0.2$, the binding energy remained constant at 400.1 eV. The shift of N 1s peak toward a lower binding energy for the NO adsorbed on the K-covered surface is explained by the work function changes [7]. However, the NO adsorption sites on the K-deposited surface have not been clarified.

To clarify the NO adsorption sites on the K/Pd(1 1 1) surface, we examined the sites using IRAS. Fig. 2 shows the IRA spectra measured after the saturated adsorption of NO on the K/Pd(1 1 1) surface ($\Theta_K = 0–0.54$) at 320 K. The peak for NO adsorbed on the threefold hollow site of Pd was observed at 1545 cm$^{-1}$ for the clean Pd(1 1 1) surface [11]. For the K/Pd(1 1 1) surface, three peaks for adsorbed NO were observed at 1495–1523 cm$^{-1}$ (i), 1392–1412 cm$^{-1}$ (ii), and 1348 cm$^{-1}$ (iii). The intensity of peak (i) decreased with K coverage, clearly indicating that the peak was due to NO adsorbed on Pd (NO–Pd). Peaks (ii) and (iii) appeared only on the K-deposited surface, which indicates that they were correlated with the deposited K. Using IRAS, Bender et al. [15] observed two peaks, at 1270 and 1325 cm$^{-1}$, for NO adsorbed on a Na-deposited Cr$_2$O$_3$(0 0 0 1)/Cr(1 1 0) surface, and these peaks arise from NO adsorbed on Na in different chemical environments. It is considered that peaks (ii) and (iii) are likewise due to NO adsorbed on K in different chemical environments.

Fig. 3 shows the intensities of the three IRAS peaks observed for the K/Pd(1 1 1) surface as a function of K coverage. The intensity of peak (i), which was due to the NO–Pd, decreased linearly with K coverage and reached zero at $\Theta_K = 0.24$, which indicates that the number of Pd atoms exposed at the surface decreased with K coverage. The intensity of peak (ii) increased with K coverage up to approximately 0.2 and then gradually decreased, and this result indicates that the Pd and K atoms worked cooperatively as adsorption sites.
for NO. Therefore, it is interpreted that peak (ii) was due to NO adsorbed on the interface of the Pd–K island (NO-interface). Peak (iii) was observed at around $\Theta_K > 0.2$, and its intensity increased as the intensity of peak (ii) decreased. This behavior indicates that peak (iii) was due to NO adsorbed on the surface of the K island (NO–K).

3.2. NO decomposition

We investigated the thermal behavior of NO adsorbed on the K/Pd(1 1 1) surface by TPD. Fig. 4 shows the TPD spectra of $^{15}$N$_2$ ($m/e = 30$), $^{15}$NO ($m/e = 31$) and $^{15}$N$_2$O ($m/e = 46$) after the saturated adsorption of NO on the K/Pd(1 1 1) surface at 320 K. No desorption peaks of O$_2$ or NO$_2$ were observed. For the clean Pd(1 1 1) surface, we observed the desorption peak of NO at 550 K [11] and small desorption peaks of N$_2$ and N$_2$O at 530 K which were due to the NO dissociation on the defect sites [16]. In contrast, we observed significant N$_2$ desorption from K-deposited Pd(1 1 1) surfaces at 530 K for entire range of K coverage. This result clearly indicates that NO dissociation sites were created by the deposition of K. At $\Theta_K$ values greater than 0.24, another N$_2$ desorption peak was observed, at 610 K, in addition to the one at 530 K: that is, NO decomposition proceeded at two different temperatures on the K/Pd(1 1 1) surface. On the other hand, NO was observed to desorb at around 530 K at $\Theta_K < 0.24$. At $\Theta_K > 0.24$, a new desorption peak appeared at 700 K in addition to the peak at 530 K, indicating that NO adsorption was stabilized by K [7].

Fig. 3. IRAS peak intensities for the K/Pd(1 1 1) surface as a function of K coverage.

Fig. 4. TPD spectra of (a) $^{15}$N$_2$ ($m/e = 30$), (b) $^{15}$NO ($m/e = 31$) and (c) $^{15}$N$_2$O ($m/e = 46$) after the saturated adsorption of NO on the K/Pd(1 1 1) surface at 320 K.
It has been reported that although NO does not dissociate on clean Pt(111), it does dissociate on K-deposited Pt(111) surfaces at temperatures higher than 300 K [7]. The K-promoted NO dissociation can be explained by an increased back-donation of surface electrons into the $2\pi$ molecular orbital of NO. The decomposition behavior of NO on the K-promoted Pt(111) surface has been investigated using TPD [8]. The desorption of N$_2$ and N$_2$O is observed. The former peaks are observed at around 400 and 600 K. For the decomposition of NO on a Na-deposited Ag(111) surface, the desorption of N$_2$ is observed at around 500 and 600 K [10]. The N$_2$ desorption at around 600 K is described to be dependent on the level of subsurface Na and O contamination. However, the reason for the two N$_2$ temperatures has not been explained in detail; that is, the relationship between the adsorption sites and the decomposition sites of NO has not yet been clarified.

The amount of N$_2$ desorption as a function of K coverage for our K/Pd(111) system is plotted in Fig. 5. The total amount of N$_2$ desorption over the K/Pd(111) surface increased with K coverage when $\Theta_K < 0.2$ and then remained constant when $\Theta_K > 0.2$. The amount of N$_2$ desorption at 530 K increased with K coverage when $\Theta_K < 0.2$ and then gradually decreased when $\Theta_K > 0.2$. This result, which is consistent with that for the intensity of the NO-interface peak (Fig. 3), indicates that the N$_2$ desorption at 530 K was due to the dissociation of NO-interface. The amount of N$_2$ desorption at 610 K increased with K coverage when $\Theta_K > 0.2$. The relationship between the amount of N$_2$ desorption at 610 K and K coverage was similar to that between the intensity of the NO–K peak and K coverage as shown in Fig. 3. On the other hand, the NO adsorption site could not be determined from NO desorption peaks, because it is undecided whether the NO adsorption site could be attributed to the NO–K desorption.

To confirm the thermal behavior of NO–K, we examined the adsorption species on the K/Pd(111) surface ($\Theta_K = 0.52$) using IRAS. The surface was prepared by flashing to 540 K in a vacuum after the saturated adsorption of NO at 320 K (Fig. 6). Two peaks were observed, at 1283 and 1468 cm$^{-1}$. The peak at 1283 cm$^{-1}$ was due to the NO–K; this value was 65 cm$^{-1}$ lower than that obtained after the saturated adsorption of NO at 320 K. We found that the NO–K peak at 320 K shifted by 95 cm$^{-1}$ depending on the peak intensity. Using
literature data [17], we identified the peak at 1468 cm\(^{-1}\) as a NO\(_2\) species. We confirmed that the NO\(_2\) was formed by the co-adsorption of NO and O on the K/Pd(1 1 1) surface at 320 K, where the NO\(_2\) peak was observed at 1465–1475 cm\(^{-1}\). This is in good agreement with the peak frequency observed for the K/Pd(1 1 1) surface after flashing to 540 K. We consider that the K–NO\(_2\) species was formed by reaction of adsorbed NO with oxygen produced by the dissociation of NO–interface.

Fig. 7 shows the TPD spectra of \(^{15}\)NO \((m/e = 31)\) and \(^{15}\)N\(_2\) \((m/e = 30)\) on the K/Pd(1 1 1) surface \((\Theta_K = 0.52)\) flashed to 540 K with a 1 K/s heating rate in a vacuum after the saturated adsorption of NO at 320 K.

4. Conclusions

(1) Three different NO adsorption sites were found on the K-deposited Pd(1 1 1) surface: the Pd site, the interface of the Pd–K island, and the surface of the K island.

(2) The adsorption of NO on the clean Pd(1 1 1) surface was purely molecular and reversible, whereas the decomposition of NO proceeded only on the K-deposited Pd(1 1 1) surface.

(3) The NO adsorbed on the interface of the Pd–K island and on the surface of the K island decomposed to N\(_2\) at 530 and 610 K, respectively.

References