〈연구논문〉

The Effects of Defect Sites on the Dissociation of NO on Pt(111) Surface

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Pt(111) 표면에서 NO의 해리에 미치는 표면결함의 영향

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Abstract — Adsorption of nitric oxide on the Pt(III) surface sputtered by Ar-ion has been studied using thermal desorption spectroscopy and Auger electron spectroscopy. Ar-ion sputtering creates defect sites on the Pt(111) surface to promote dissociation of NO. Dissociation of NO occurs through a precursor state of NO (β state) adsorbed at defect sites. The precursor state is characterized by the terminal bent species. At low coverage most of adsorbed NO dissociates. And as increasing the coverage, the fraction of dissociation remains about 80%.

요   약 — 열탈착 분광법과 Auger 전자분광법을 이용하여 Ar-이온에 스퍼터링된 Pt(111) 표면에 NO의 흡착이 연구되었다. Pt(111) 표면에 Ar-이온에 의해서 생성된 결함자리들은 NO의 해리를 촉진시켰으며 이러한 해리는 결함자리에 흡착되는 NO(β-상태)의 선구상태를 거쳐서 일어났다. 그리고 이들 상태에 흡착된 NO는 이전에 보고된 굽힘진동을 하는 화학종이라고 규정하였다. NO의 낮은 덮힘율에서는 흡착되는 NO의 대부분이 해리되며, 덮힘율이 증가함에 따라 해리되는 분율은 약 80%로 일정하였다.

1. Introduction

Because the catalytic oxidation and reduction of NO_x has considerable practical importance in the elimination of toxic automotive exhaust, the interactions of nitric oxide with platinum metal surfaces have been extensively studied in the past by using various surface spectroscopic techniques. This system is also of interest because of very similar electronic structures between CO and NO. The only dif-

ference is that NO possesses an unpaired electron in the antibonding 2π orbitals, which is the reason for more complex properties of the chemisorption of NO than those of CO. For instance, under the conditions of UHV pressure and room temperature it is known that CO adsorbs and desorbs molecularly on clean platinum(111) surface [1, 2]. Nitric oxide under the similar conditions, on the other hand, adsorbs molecularly and/or dissociatively depending on surface orientations [3-16]. The onset

of the NO dissociation can be easily identified by the appearance of decomposition products such as nitrogen and oxygen.

Gorte *et al.* [7] reported that the desorption spectra from Pt(111), (110) and (100) show different shapes and different peak temperatures. In their report, the desorption activation energies for th major tightly bound states on the (100), (110) and (111) plane are 36, 33.5 and 25 kcal/mol, respectively. And the fraction of dissociation is less than 2% on the Pt (111) surface. Ertl *et al.* [9] also studied the interaction of NO with Pt(111) surface using molecular beam technique and thermal desorption spectroscopy (TDS), and reported that the molecular adsorption predominates. They reported the NO dissociation is restricted to defect sites and the activation energy for desorption and the pre-exponential factor are 33.1 kcal/mol and $10^{15.5}$/sec, respctively.

In a more recent study, Agrawal and Trenary [16] have used an infrared reflection-absorption spectroscopy (IRAS) to characterize NO at defect sites. The adsorbed molecules at the defect sites show IR bands in the range of $1820 \sim 1840\ cm^{-1}$, a characteristic of a linear Pt-N-O configuration, while a bent Pt-N-O configuration has the bands in $1609 \sim 1634\ cm^{-1}$. Other IR bands are assigned to NO at the terminal ($1700 \sim 1720\ cm^{-1}$) and at the two-fold bridge sites ($1475 \sim 1500\ cm^{-1}$) of the (111) terraces.

In this paper, we compare the adsorption and the desorption of NO on the normally flat (111) surface and the Ar-ion induced defect (111) surfaces using thermal desorption spectroscopy (TDS) and discuss the role of the defect sites on the decomposition of NO.

2. Experimental

The experiments were carried out in a stainless-steel ultra-high vacuum system (UHV) with the base pressure near 5×10^{-10} torr. The UHV chamber is equipped with a quadrupole mass spectrometer (VG: 200 amu) and a 4-Grid LEED optics for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES).

Additional features are an argon ion gun for sur-

face cleaning, an ionization gauge for measuring pressure, and a manipulator for *x, y, z* motion of the sample. More details of the system were found in previous publications [17, 18].

The platinum single crystal (111) used in the experiments was approximately 10 mm in diameter and 1 mm in thickness. It was spotwelded onto a pair of W wire (~ 0.25 mm), which were themselves spotwelded onto a pair of parallel Mo leads (1.5 mm is diameter). These rods were directly connected to a pair of Cu blocks, which were also connected on an electrical feedthrough, for the crystal to be heated resistively. A chromel-alumel thermocouple was sportwelded to the edge of the crystal for temperature measurements.

The Pt(111) crystal was first cleaned using a circle of Ar^+ ion bombardment in the range of 300 and 600 K, followed by annealing at 1300 K. Once cleaned in this treatment, a short period of ion bombardment or the treatment of low temperature oxygen (1×10^{-7} torr at 700 K for 3 min) followed by then brief heating to 1300 K were sufficient to obtain a well ordered clean surface, which was identified by LEED and AES. The defect sites on Pt (111) were induced by Ar-ion sputtering before being heated to 700 K to remove adsorbed species of the residual gases.

Thermal desorption spectra TDS were taken by placing the Pt crystal in a line of sight with the mass spectrometer ionizer. The crystal was heated at a rate of about 10 K/sec by passing direct current through it. A multiple ion mode in mass spectrometer was used for the simultaneous detection of different species desorbed from the sample. Signals corresponding to C and N were also monitored during the experiments in order to distinguish between N_2 and CO.

3. Results and Discussion

Fig. 1. shows a sequence of thermal desorption spectra (TDS) for NO adsorbed on the Pt(111) surface at 300 K as a function of NO exposure. A nearly symmetric about 460 K (denoted as β) is negligibly small. Even though at a glance th shape of this spectra for the α state looks somewhat different from
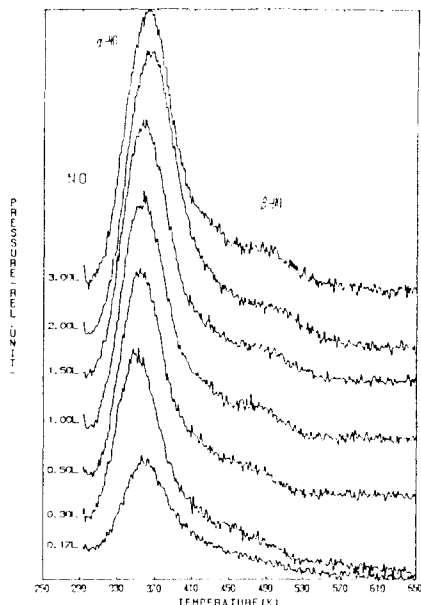
Fig. 1. Desorption spectra for NO on Pt(111) surface as a function of NO exposures.

Fig. 2. Thermal desorption spectra for NO on Ar-ion sputtered Pt(111) as a function of NO exposure.

the results reported previously [7, 9, 20], which was showed an asymmetric peak due to partial overlap of two peaks in the range of 300 to 400 K, it is consistent with one of them ovserved at low coverages. Because no peak shift is observed with increasing coverage, it suggest a first-order desorption kinetics. Using the method by Redhead [19] and 10^{16} sec^{-1} as a value of the pre-exponential factor [7, 9] the desorption activation energy is estimated to be 28 kcal/mol, which is also in well agreement with previous results [7,9].

The results of vibrational spectroscopy [13, 15, 16] indicate that NO adsorbs molecularly on the Pt(111) surface at all coverages. At low coverages, the adsorbed NO was characterized by a band near 1500 cm^{-1}, which corresponds to the adsorbed species at two-fold bridge sites. It was stable to 318 K. In contrast, a band near 1700 cm^{-1} for the NO adsorbed at higher coverage was assigned to the on-top linearly bonded molecule. It disappeared above that temperatures. Thus based on these vibrationa spectroscopic results it could, be suggested that the α state almost consists of NO adsorbed molecularly at the bridge site on the uniform Pt(111).
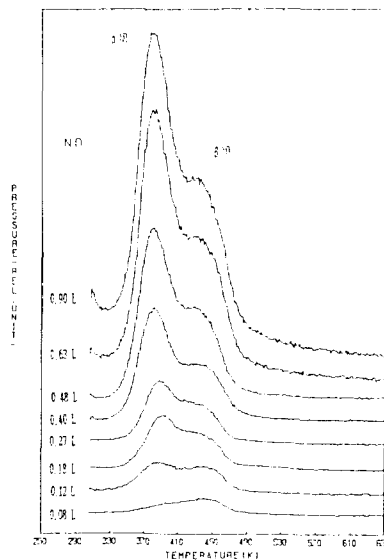
During the TDS measurement, we also tried to obtain the spectra for N_2 that might indicate dissociation of NO on the surfaces, but they were nearly not observed. This implies that the dissociation of NO does not occur on the well annealed surface. Ertl et al. studied for the kinetics of NO adsorption on the Pt(111) surface using molecular technique and TDS, and they suggested that the peak assigned to the β state is due to the defect sites on the surface and the dissociation of NO is restricted to the defect sites, the number of which is negligibly small on the perfect surface.

In order to investigate the effects of defect sites on the dissociation of NO, the TDS measurement for the NO adsorption on an Ar-ion sputtered Pt (111) was performed. Fig. 2 shows a series of thermal desorption spectra as a function of NO exposure following the adsorption of NO on the Ar-ion sputtered Pt(111) surface at 300 K. Apart from the peak maximum of NO at 380 K observed for the uniform Pt(111), a second maximum at 450 K is observed at all exposures, which appeared only as a trace for the well-annealed uniform surface as shown in Fig. 1. As the coverage increases, the intensities of both peaks grow continuously. It is evident that the

at this temperature. Peak maximum in the β state as well as in the α state also exhibits no marked shift with the increasing coverage. And the evaluated desorption energy is 33 kcal/mol.

In a more recent study, Agrawal and Trenary [16] used IR spectroscopy to characterize NO adsorption at the defect sites on Pt(111) surfaces and argues that the observed two stretching bands in the range of 1609~1634 cm⁻¹ and 1820~1840 cm⁻¹ are due to a terminal bent and a linear configuration adsorbed at the defect sites, respectively. They also reported that the bent species appears at higher temperature than the linear configuration does. Hence, it suggests that the β state observed here be characterized by these two species, although the energy states of those species are not seperated by TDS. This also explains why the β state shows the more broad peak in TDS than the α state corresponding to the uniform surface.

Fig. 3 shows a set of TDS of N_2 taken simulataneously with those of *Fig.* 2. Similar to the NO desorption, there are two NO peaks at 390 and 470 K which are higher temperatures by 10 and 20 K than those for the NO desorption. Although several scans were run to check for CO contamination, the desorption spectrum at 12 amu, which is expected in the case of the fragmentation of CO, showed no peak, and the spectrum run at 14 amu was simply a sum of the NO and N_2 spectra. It is convinced that these two peaks at 390 and 470 K are from the desorption of N_2. The two NO peaks will also be referred to the α state and β state, respectively. The α and β states grow sequentially with NO exposure. Desorption of N_2 for NO adsorption of no Pt surface has also been observed from several samples of other than (111) plane (7.9.21.23). In any case, the dissociation of NO was observed with appearance of the higher binding state of NO similar to the β state observed here. Thus, we conclude that the dissociation of NO occurs on the Ar-ion sputtered Pt(111) surface and that the β state observed here has a close relation to the dissociation of nitric oxide.

The N_2 spectra are similar in shape to the desorption peak at 470 K obtained from the polycrystalline platinum, which display a sharp peak with
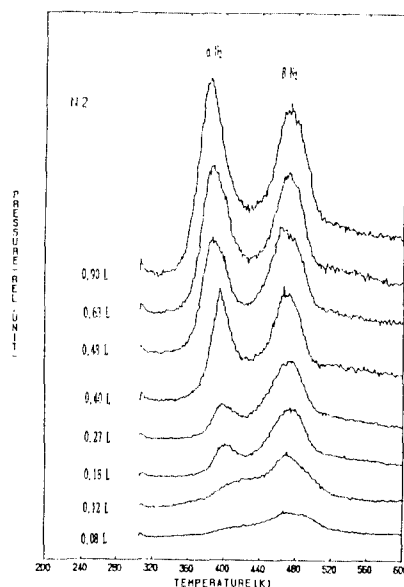

Fig. 3. Thermal desorption spectra for N_2 on Ar-ion sputtered Pt(111) as a function of NO exposure.
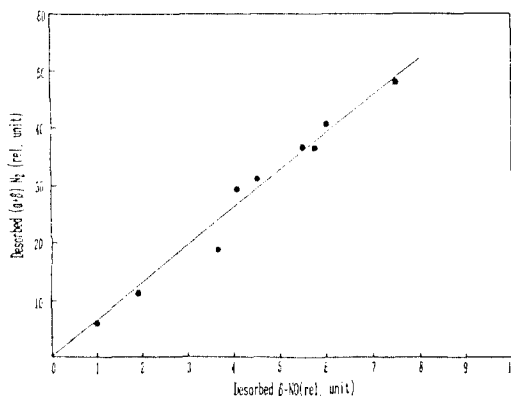

Fig. 4. Amount of desorbed N_2 as a function of the amount β-NO.

shoulder at 350 K, and to the desorption peak observed at 390 and 510 K from the Pt(100) surface. The one except is the lower isntensity on the low temperature side in the Pt(100) spectra than in the α state observed here. Thus, the N_2 desorption peak in the α state is probably due to the uniform surface and the β state comes from the defect sites induced by Ar-ion sputtering. If so, the appearance of the α state from the uniform surface implies that atomic

nitrogen produced by the dissociation of NO from Ar-ion sputtering creates the defect sites to markedly influence the β state of NO. At the lowest exposure, this state is more predominantly populated than the α state as one would expect for NO desorption from defect sites. This indicates that a diffusion barrier is surfficiently low for the adsorbed nitrogen oxide to diffuse into a higher energy state the defect sites diffuses onto the uniform surface before it desorbs there, even though it seems implausible. The reason is that no dissociation of NO occurs on the uniform surface.

Fig. 4 shows the amount of the total nitrogen desorbed from the α and the β states as a function of NO population in the β state. As shown in Fig. 4, the total amount of N_2 is proportional to the population of NO in the β state. This implies that the dissociation of NO occurs as a fraction of the β state and that it directly depends on the β state. Hence the dissociation probability of NO is calculated from the following equation,

$$P(\%) = \frac{2\alpha(N_2) + 2\beta(N_2)}{\beta(NO) + 2\alpha(N_2) + 2\beta(N_2)} \times 100$$

Where $\alpha(N_2)$ and $\beta(N_2)$ are the peak area of N_2 in α and β states, respectively, while $\beta(NO)$ is the peak area of NO in β state.

Fig. 5 shows the dissociation probability of β-NO as a function of NO exposure. At initial coverage most of NO in the β state dissociates (about 90%) and at the higher exposure the dissociation probability remains 80%.

Our results for the desorption and the dissociation of NO are compatible to those for polycrystalline Pt(21), Pt(100) and Pt(110) [7] and Pt single crystal with various step sites [21-23]. After the saturation of NO, no dissociation of NO was observed on Pt(111), in good agreement with our result. On Pt(100), three NO desorption states including the one for a broad peak at 500 K form and the 50% dissociation was observed, while a narrow NO desorption peak at 470 K was shown on Pt(110) and the 15% dissociation was observed. Banhalzer *et al.* [22] found that the amount of the NO dissociation depends strongly on the crystal face used. Pt(410) is unusually active for the NO dissociation (about
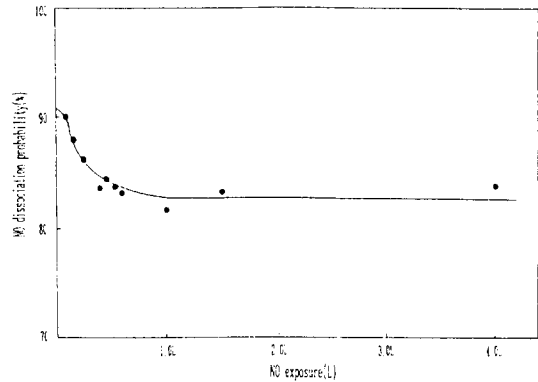

Fig. 5. Dissociation probability of β-NO as a function of NO exposure.

100%) [23] and Pt(100), Pt(111) and Pt(211) have very similar reactivities for the NO dissociation [24]. Our Ar-ion sputtered Pt(111) surface is very similar to Pt(211) surface, when compared to the shape and the behavior of desorption spectra for N_2 and NO. Thus, we suggest that our sputtered Pt surface has a structure similar to the Pt(211) surface, which consists of (100) terraces and (111) step. It is plausible because the regular Pt(111) surface will be resulted even after Ar-ion sputtering. Most of portions sputtered by Ar-ion will show structure like the reconstructed Pt(100), which have been observed after well annealing of Pt(100).

As mentioned earlier, on the basis of vibrational spectroscopic data [16], the β state of NO observed here is described with the terminal linear and the bent species. The detailed analysis for these data also indicats that at low coverage the bent species appear predominantly at 300 K and the terminal linear species grow continuously with increasing coverage. On the other hand, our results for the dissociation probability of NO show that most of NO species in the β state dissociate at initial coverage. Thus, we conclude that the terminal bent species in the β state of NO contribute to the dissociation of NO. This argument agrees with what one would expect from the NO dissociation on the surface.

4. Conclusion

A thermal desorption spectra obtained for the

uniform Pt(111) saturated with NO at 300 K indicates that the chemisorption of nitric oxide on the Pt(111) is predominantly molecular, which is characterized by a two-fold bridge site species and a terminal linear one reported previously. Ar-ion sputtering creates defect sites on the Pt(111) surface to promote dissociation of NO, which occurs through a precursor state of NO adsorbed at the defect sites. The adsorption energy for NO adsorbed at the defect sites is estimated to be 33 kcal/mol, which is higher 5 kcal/mol than that on the uniform surface. At low coverage most of the adsorbed NO dissociates. And as increasing the coverage, the fraction of dissociation remains 80%. On the basis of vibrational spectroscopic data reported previously, the NO state appeared at the defect sites is characterized by two types of species, terminal linear and bent. And it is also argued that the bent species is contributes to the dissociation of NO.

Acknowledgement

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