Two kinds of adsorbed N atoms with different reactivities with H_2 on a $Pt_{0.25}Rh_{0.75}(100)$ surface

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Two kinds of adsorbed N atoms exist on a $Pt_{0.25}Rh_{0.75}(100)$ surface. One desorbs at 490 K and the other desorbs at 650 K. The former reacts with H_2 at 400 K, but the latter does not. It is supposed that the adsorption of these two N atoms is responsible of the surface composition, ratio of Pt and Rh.

Keywords: platinum, rhodium, alloy, surface composition, nitrogen, oxygen

1. Introduction

PtRh-alloy single-crystal surface has been extensively studied from the viewpoint of model catalyst for a three-way catalyst [1–18] which is developed as an environmental protection by removing NO_x, CO and hydrocarbons from automotive exhaust gas. One important feature of the PtRh-alloy surface is a flexibility on surface composition depending on ambient gas, that is, the fraction of Pt and Rh is changed at temperature higher than 900 K in vacuum but at ca. 400 K and higher than that in NO or O_2 [1–6,16]. Tsong et al. [1,2] showed by using FIM that the (111) as well as (100) surfaces of PtRh-alloy tip annealed at 1000 K are composed of the Pt-enriched topmost layer and the Pt-depleted (Rh-enriched) second layer. When a PtRh(100) surface is heated in O_2, Rh atoms are extracted at 400 K, and the LEED pattern changes from (1×1) to $p(3 \times 1)$-O [7,11] or $c(2\times 20)$-O [17]. Powell and Chen [18] found the segregation of Pd and Rh for a dispersed Pd–Rh–Pt catalyst after the use for vehicle.

As a model of bimetallic catalyst, Pt-electrodeposited Rh single-crystal surfaces and Rh-electrodeposited Pt single-crystal surfaces were extensively studied in a UHV chamber attached to an electrochemical cell [19–24]. These results showed that the surface structure as well as the surface composition of these bimetallic surfaces are readily changed by heating in O_2 or NO or $NO + H_2$. Both reconstructed surfaces of Pt/Rh(100) and Rh/Pt(100) take a similar structure to a PtRh(100)-alloy surface reconstructed at 500 K in O_2 or NO. As a result, the Pt/Rh(100), Rh/Pt(100) and PtRh(100) reconstructed surfaces have an equal catalyst activity for the reaction of $NO + H_2$, which indicates that the surface reconstruction during catalysis is responsible for the catalytic activation of this PtRh three-way catalyst [7,8,11,12,15,25].

When a reaction of $NO + H_2$ is performed on a PtRh (100) surface under suitable conditions, O atoms preferentially react with H_2, so that N atoms are accumulated on the surface to form a $c(2 \times 2)$-N structure [20–23]. The accumulation of adsorbed N atoms on a $Pt_{0.25}Rh_{0.75}(100)$ surface can also be made by the reaction of $NO + CO$, which results in a $c(2 \times 2)$-N LEED pattern [27].

In this paper, we report the formation of two kinds of N atoms, both exhibiting a $c(2 \times 2)$-N LEED pattern, on a $Pt_{0.25}Rh_{0.75}(100)$-alloy surface depending on the surface composition. These two kinds of N atoms have different desorption temperatures, one is 490 K and the other is 650 K, and different reactivities with respect to H_2 at 400 K.

2. Experimental

Experiments were performed in a UHV chamber (base pressure less than 4×10^{-10} Torr) attached to a high-pressure reaction cell (base pressure less than 2×10^{-9} Torr) [26]. The UHV chamber is equipped with a low-energy electron diffraction (LEED) optics, an Auger electron spectrometer (AES) and a quadrupole mass spectrometer (Q-MS). A $Pt_{0.25}Rh_{0.75}(100)$ sample was mechanically polished down to 0.25 μm grain size using standard techniques. The sample was spot-welded onto a Ta filament which could be heated up to 1400 K by Joule heating. The temperature was measured by a chromel/alumel thermocouple spot-welded to the side of the sample. After introducing the sample into the UHV chamber, the sample was cleaned by cycles of Ar^+ ion bombardment, oxidation with 1×10^{-7} Torr of O_2 at 1200 K for 15 min and annealing at 1200 K for 15 min until the surface of the sample was free of contamination detected by AES. This procedure resulted in a sharp (1×1) LEED pattern. Then the surface composition was adjusted to $Pt/Rh = 0.8$ by heating at 1200 K for 15 min in vacuum and subsequent quick quenching to room temperature. Thermal desorption spectroscopy (TDS) was recorded by a recorder (Graphtec WX 1000).

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3. Results

As the composition and the structure of a $Pt_{0.25}Rh_{0.75}$ (100) surface are flexible on the pretreatment, in this paper we termed PtRh surfaces as follows:

Surface I: a clean $Pt_{0.25}Rh_{0.75}$(100) surface (Pt-enriched), the surface composition is Pt/Rh = 0.8 measured by AES;

Surface II: a p(3 × 1)-O $Pt_{0.25}Rh_{0.75}$(100) surface (Rh-enriched) prepared by exposing a clean $Pt_{0.25}Rh_{0.75}$(100) surface to 1×10^{-7} Torr O_2 at 600 K for 5 min, the surface composition is Pt/Rh = 0.2 measured by AES;

Surface III: a c(2 × 20)-O $Pt_{0.25}Rh_{0.75}$(100) surface (Rh-enriched) prepared by exposing a clean $Pt_{0.25}Rh_{0.75}$(100) surface to 8×10^{-5} Torr O_2 at 600 K for 2 min, the surface composition is Pt/Rh = 0–0.07 measured by AES;

Surface IV: a $Pt_{0.25}Rh_{0.75}$(100) surface (Rh-enriched) prepared by exposing a p(3 × 1)-O $Pt_{0.25}Rh_{0.75}$(100) surface to 1×10^{-8} Torr H_2 at room temperature for 15 min to remove the adsorbed oxygen, the surface composition is Pt/Rh = 0.2 measured by AES;

N(l): N atoms accumulated on a $Pt_{0.25}Rh_{0.75}$(100) surface by a reaction of 1×10^{-8} Torr NO + 1×10^{-8} Torr CO at 400 K for 15 min, they desorb at 490 K and react with H_2 at 400 K;

N(h): N atoms accumulated on a $Pt_{0.25}Rh_{0.75}$(100) surface by a reaction of 1×10^{-8} Torr NO + 1×10^{-8} Torr CO at 550 K for 15 min, they desorb at 650 K and do not react with H_2 at 400 K.

3.1. N atoms accumulated on $Pt_{0.25}Rh_{0.75}$(100) clean surface

When a clean $Pt_{0.25}Rh_{0.75}$(100) surface (surface I) was exposed to 1×10^{-8} Torr NO + 1×10^{-8} Torr CO at 400 K for 15 min, accumulation of N atoms was brought about and a c(2 × 2) LEED pattern, as shown in figure 1(a), appeared. The surface composition used in this experiment was Pt/Rh = 0.8 by AES. TDS of this c(2 × 2)-N surface showed a desorption peak at 490 K (figure 2(a)). From figure 2(b) it is clear that the TDS peak in figure 2(a) can be attributed to the desorption of N_2 other than CO. This kind of adsorbed N atoms is described by N(l) in this paper.

After an exposure of this c(2 × 2)-N surface to 1×10^{-7} Torr H_2 at 400 K for 15 min, the (1 × 1) LEED pattern was resumed and the TDS presented no desorption of N_2 (figure 2(c)). This result evidently shows that the N(l) is removed by a reaction with H_2.

When the surface I was exposed to 1×10^{-8} Torr NO + 1×10^{-8} Torr CO for 15 min at 550 K instead of 400 K, LEED also presented a c(2 × 2) pattern (figure 1(b)). The TDS (figure 3(a)) of this surface showed the desorption of N_2 at 650 K proved in figure 3(b). This kind of adsorbed N atoms is decided by N(h). After 1×10^{-7} Torr H_2 was introduced to the N(h) accumulated $Pt_{0.25}Rh_{0.75}$(100) surface at 400 K for 45 min, the c(2 × 2) of LEED pattern was still observed, and TDS (figure 3 (c) and (d)) proved the existence of N(h) after the treatment with H_2.

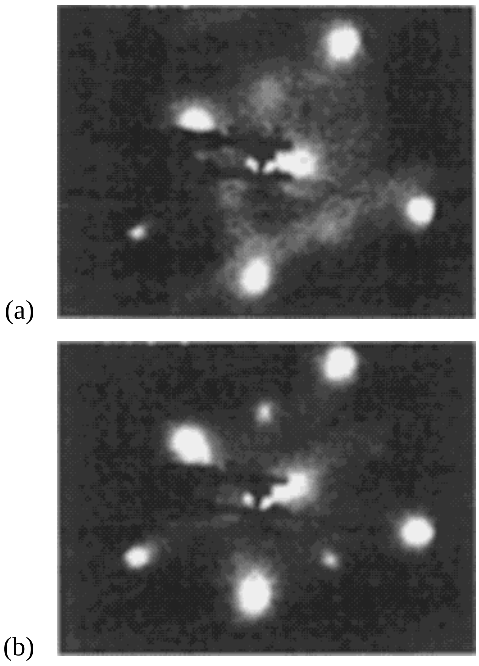

Figure 1. (a) A c(2 × 2)-N LEED pattern obtained by introducing 1×10^{-8} Torr NO + 1×10^{-8} Torr CO to surface I at 400 K for 15 min. Electron beam energy = 67 eV. (b) A c(2 × 2)-N LEED pattern prepared by exposing 1×10^{-8} Torr NO + 1×10^{-8} Torr CO to surface I at 550 K for 15 min. Electron beam energy = 67 eV.

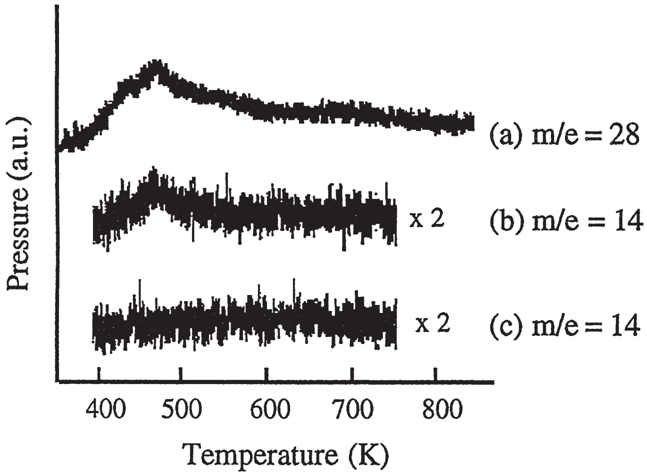

Figure 2. TDS spectra of (a) $m/e = 28$ and (b) $m/e = 14$ from a c(2×2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface prepared by introducing 1×10^{-8} Torr NO + 1×10^{-8} Torr CO to surface I at 400 K for 15 min, and (c) $m/e = 14$ after the c(2 × 2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface of (a) was exposed to 1×10^{-7} Torr H_2 at 400 K for 15 min. The desorption peak of N_2 at 490 K disappeared after introducing H_2.

These results suggest that two kinds of adsorbed N atoms, low-temperature nitrogen (N(l)) and high-temperature nitrogen (N(h)), are formed on the surface I by performing a reaction of NO + CO at different temperatures. The N(l) undergoes a desorption at 490 K and reacts with H_2 at 400 K, the N(h) desorbing at 650 K does not react with H_2 at 400 K. As it will be discussed below, an increase of Rh on the alloy surface is responsible for the formation of the N(h).

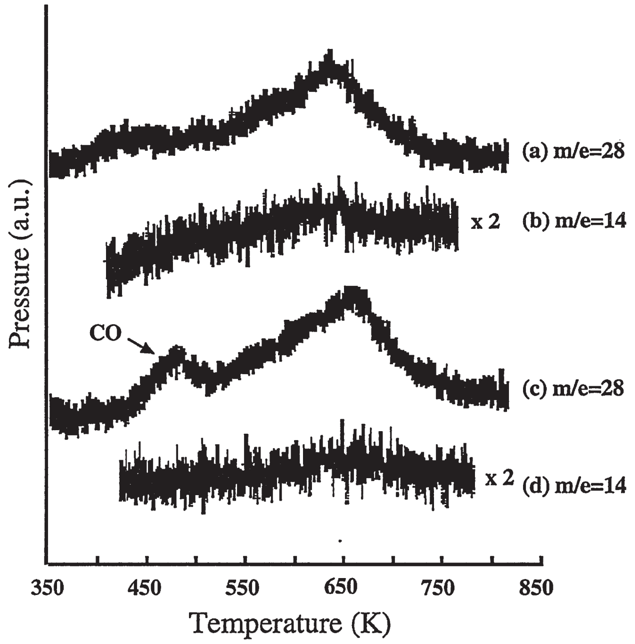

Figure 3. (a) TDS spectrum of $m/e = 28$ from a c(2 × 2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface prepared by introducing 1×10^{-8} Torr NO + 1×10^{-8} Torr CO to surface I at 550 K for 15 min. (b) ($m/e = 14$) confirms that the adsorption peak in (a) is due to the formation of N_2. (c) TDS spectrum of $m/e = 28$ obtained from a PtRh surface prepared by introducing 1×10^{-7} Torr H_2 to the surface of (a) at 400 K for 15 min. (d) confirms that the desorption peak of N_2 at 650 K still exists after introducing H_2 and the desorption peak at ca. 490 K in (c) is attributed to the formation of CO.

To confirm that the desorption peak at 490 K can be attributed to N_2, ^{15}NO was used to remove the ambiguity of overlapped CO ($m/e = 28$). When a surface II (Rh-enriched surface) was exposed to 1×10^{-7} Torr $^{15}NO + 1 \times 10^{-6}$ Torr CO for 2 min at 400 K, the accumulation of ^{15}N was confirmed by a c(2 × 2)-N LEED pattern. In this case, the TDS presented two desorption peaks of $^{15}N_2$ corresponding to the N(l) and the N(h) (figure 4(a)). It is noteworthy that the c(2 × 2)-N LEED pattern did not disappear after treating with 1×10^{-7} Torr H_2 at 400 K for 15 min, and this surface gave a high-temperature desorption peak of $^{15}N_2$ (figure 4(b)). On the surface II, the two desorption peaks of $^{15}N_2$ covered almost equal areas, as shown in figure 5(a), that is, the amounts of N(l) and N(h) are almost equal on this surface.

3.2. *N atoms accumulated on p(3 × 1)-O or c(2 × 20)-O $Pt_{0.25}Rh_{0.75}$(100) surface*

When a surface I is exposed to O_2, a p(3 × 1)-O or c(2 × 20)-O structure is formed depending on the exposure of O_2 and temperature [11,17,18,20,22,25,26]. By performing a reaction of NO + CO on the p(3 × 1)-O surface (surface II) or the c(2 × 20)-O surface (surface III) of $Pt_{0.25}Rh_{0.75}$(100), N atoms are also accumulated.

In this experiment, a surface II was prepared by exposing a surface I to 1×10^{-7} Torr O_2 at 600 K for 5 min, where Rh atoms were segregated on the surface, as reported previously [7,11], and the surface composition became Pt/Rh = 0.2 by AES. Then a mixture of 1×10^{-8} Torr NO + 1×10^{-8} Torr CO was introduced to the surface II at 400 K for 15 min. The p(3 × 1)-O pattern disappeared by reducing with CO, while a c(2 × 2) pattern appeared. When this surface was heated up, two TDS desorption peaks appeared, at 490 and 650 K, as shown in figure 5(a). The two desorption peaks were proved to be N_2 as shown in figure 5(b). When the nitrogen-adsorbed surface was heated in 1×10^{-7} Torr H_2 for 45 min at 400 K, the desorption peak at 490 K disappeared in the TDS, and only the desorption peak of N_2 at 650 K was observed (figure 5 (c) and (d)), that is, the N atoms desorbing at 490 K were selectively removed by reacting with H_2. By comparing the result on the surface I, it is clear that both the N(l) and the N(h) are simultaneously formed on the surface II, and only the N(l) reacts with H_2 at 400 K, but the N(h) does not, which is identical to the result on the surface I.

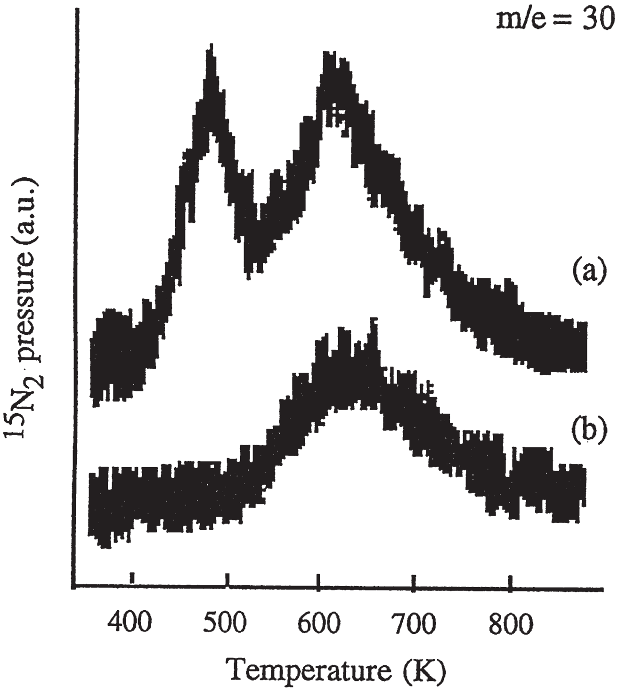

Figure 4. TDS spectra of $m/e = 30$ ($^{15}N_2$) obtained from (a) a c(2 × 2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface prepared by introducing 1×10^{-7} Torr $^{15}NO + 1 \times 10^{-6}$ Torr CO to surface II at 400 K for 2 min, and (b) after the surface of (a) was exposed to 1×10^{-7} Torr H_2 at 400 K for 15 min. It is clear that the nitrogen desorbed at 490 K has a reactivity with H_2, but the nitrogen desorbed at 650 K does not react with H_2.

When a surface I is exposed to O_2 of higher pressure or for a longer time at 600–700 K, another reconstructed surface giving a c(2 × 20)-O structure is formed [17]. In our study, a c(2 × 20)-O surface (surface III) was prepared by heating a surface I in 8×10^{-5} Torr O_2 at 600 K for 2 min. The surface composition of the c(2 × 20)-O was Pt/Rh = 0–0.07 by AES. The surface III was exposed to 2×10^{-9} Torr NO + 1×10^{-8} Torr CO at 400 K for 15 min and then it reduced by exposing to 1×10^{-7} Torr H_2 gas at 400 K for 15 min. The accumulation of N atoms was

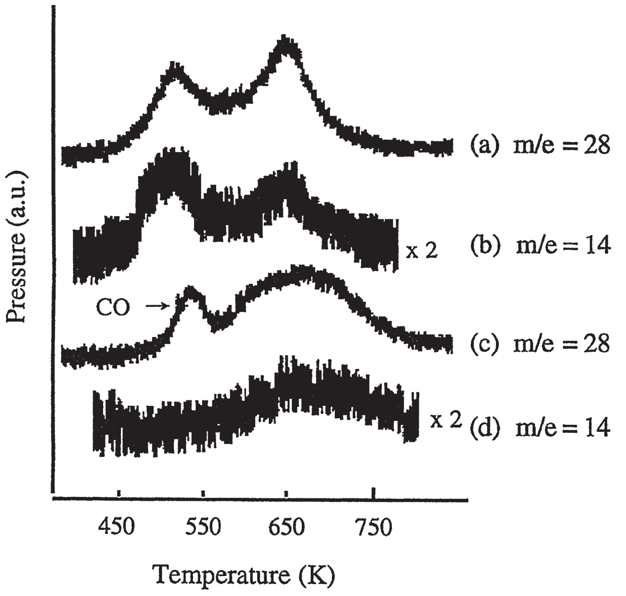

Figure 5. TDS spectra of (a) $m/e = 28$ and (b) $m/e = 14$ from a c(2×2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface prepared by introducing 1×10^{-8} Torr NO + 1×10^{-8} Torr CO to surface II at 400 K for 15 min, and (c) $m/e = 28$ and (d) $m/e = 14$ after 1×10^{-7} Torr H_2 introduced to the c(2×2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface at 400 K for 45 min. (c) and (d) indicate that the desorption peak of N_2 at 490 K disappeared after an introduction of H_2, but the desorption peak of N_2 at 650 K still existed after introducing H_2.

similar to that on the surface II, that is, the TDS showed a simultaneous formation of the N(l) and the N(h) on the surface III, and the LEED showed a c(2 × 2)-N pattern. It was confirmed that when the surface III was exposed to 2×10^{-9} Torr NO + 1×10^{-8} Torr CO at 550 K for 5 min, only the N(h) was accumulated.

Comparing the results on the Pt-enriched surface I with those on the Rh-enriched surfaces II and III, it can be supposed that the Rh atoms enriched on a $Pt_{0.25}Rh_{0.75}$(100) surface are responsible for the formation of the N(h). It should be pointed out that the adsorbed oxygen itself has little influence on the adsorption of N because the adsorbed oxygen is rapidly removed by CO or H_2 during the accumulation of N atoms. To confirm this speculation, a surface II was exposed to 1×10^{-8} Torr H_2 at room temperature for 15 min. The p(3 × 1)-O pattern of the surface II disappeared (→ surface IV), and a p(1 × 1) LEED pattern appeared [17], where no oxygen was detected by AES. The surface composition of the surface IV was the same as that of the surface II, that is, Pt/Rh = 0.2 by AES. After then, the surface IV was exposed to a glow discharge of 1×10^{-6} Torr N_2^+ ion at room temperature for 5 s and followed by annealing at 400 K in vacuum. After the glow discharge, the surface gave a c(2 × 2)-N LEED pattern and the TDS of this surface showed two desorption peaks at 490 and 650 K (figure 6(a)). It was confirmed that the N(l) formed by the glow discharge reacts with H_2, but the N(h) reacts little with H_2 at 400 K (figure 6(b)). A small peak observed at ca. 490 K in figure 6(b) may be due to the sputtered N atoms from the bulk or subsurface.

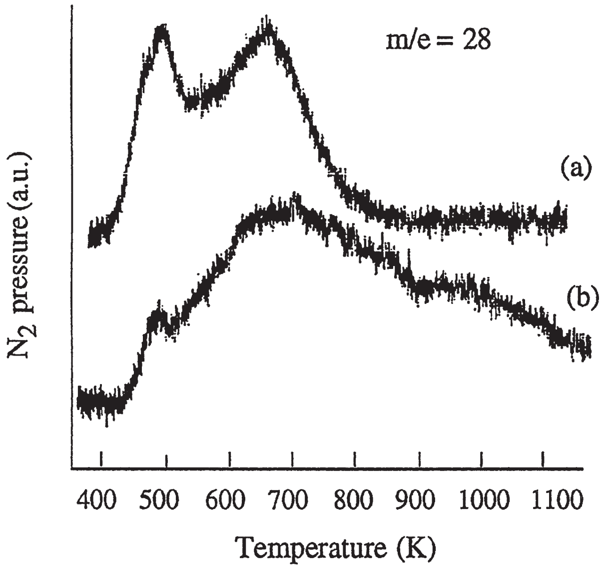

Figure 6. TDS spectra of $m/e = 28$ (N_2) obtained from (a) a c(2 × 2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface prepared by a glow discharge of 1×10^{-6} Torr N_2^+ ion at room temperature for 5 s to surface IV and followed by annealing at 400 K in vacuum, and (b) a c(2 × 2)-N/$Pt_{0.25}Rh_{0.75}$(100) surface obtained by introducing 1×10^{-7} Torr H_2 to the surface of (a) at 400 K for 15 min.

4. Discussion

It is clear from our result that the formation of N(l) and N(h) has no relation to the preadsorbed oxygen on a $Pt_{0.25}Rh_{0.75}$(100) surface. Now a question is how the N(l) and the N(h) are formed on a $Pt_{0.25}Rh_{0.75}$(100) surface. In conformity with the fact that these two kinds of nitrogen are simultaneously formed on a p(3 × 1)-O/ or c(2 × 20)-O/$Pt_{0.25}Rh_{0.75}$(100) surface (Rh-enriched) by performing the reaction of NO + CO at 400 K but only the N(l) on the surface I (Pt-enriched), the segregation of Rh atoms during the reaction of NO + CO is supposed to be responsible for this temperature dependence.

The surface composition of a clean PtRh surface is changed by annealing in vaccum [1–6,16], and a Pt-enriched PtRh-alloy surface can be got by a short-time annealing at a temperature higher than 900 K. On the other hand, the surface of $Pt_{0.25}Rh_{0.75}$(100) is readily reconstructed by heating to 400 K in O_2, where Rh atoms are markedly increased on the surface [10]. Taking account of the fact that a clean $Pt_{0.25}Rh_{0.75}$(100) surface annealed at 1000 K is composed of a Pt-enriched topmost layer and a Rh-enriched second layer, the Rh atoms are extracted from the second layer by the adsorption of oxygen, because Rh atoms has higher affinity with respect to oxygen compared to Pt atoms [3]. In this study, the surface composition of a clean surface was estimated to be Pt/Rh = 0.8, while that of the p(3 × 1)-O was Pt/Rh = 0.2, and c(2 × 20)-O was Pt/Rh = 0–0.07 by AES. When the p(3×1)-O and c(2×20)-O/$Pt_{0.25}Rh_{0.75}$(100) surfaces were exposing to H_2 at room temperature, the LEED pattern changed to the (1 × 1) pattern, but the ratio of Pt/Rh did not change. Therefore, the surface composition did not change, and the distinctive two

Table 1
Experimental result of the formation of N(l) and N(h) by performing a reaction of 1×10^{-8} Torr NO + 1×10^{-8} Torr CO on a $Pt_{0.25}Rh_{0.75}(100)$ surface. Pt/Rh is the surface composition measured by AES. T is the sample temperature in reaction.

Surface		I	II	III	IV
Pt/Rh		0.8	0.2	0–0.07	0.2
T (K)	400	N(l)	N(l), N(h)		
	500	N(l)	N(h)		

kinds of nitrogen on a $Pt_{0.25}Rh_{0.75}(100)$ surface should relate to the Pt-enriched and Rh-enriched sites.

PtRh alloy is a random alloy [28], so that the Rh atoms on a clean PtRh(100) surface (Pt-enriched surface) may have random distribution among the Pt atoms. The nitrogen adsorbed on such a Pt-enriched PtRh(100) surface may not seriously distinguish the Pt and Rh sites, because N atoms make an ordered c(2 × 2)-N structure [7]. However, it was reported that the adsorption of nitrogen on a Pt-enriched surface is much smaller than that on a Rh-enriched surface [29,30]. So far, it has been explained by the difference of the metal–nitrogen bond, that is, N–Rh bond is stronger than that of N–Pt. In fact, the desorption temperature of N_2 on a Rh-enriched surface is higher than that on a Pt-enriched surface [8].

Based on the above mention and the adsorption temperature of N(h) being higher than that of N(l), it can be supposed that the N(h) is an adsorption on the Rh-enriched sites of a clean $Pt_{0.25}Rh_{0.75}(100)$ surface, and the N(l) is that on the Pt-enriched sites. When the reaction of NO + CO is performed on a Rh-enriched p(3 × 1)-O or c(2 × 20)-O surface, both the N(l) and the N(h) are predominantly formed at 400 K. The N(l) adsorbing on Pt-enriched sites desorbs at 490 K, but the N(h) adsorbing on Rh-enriched sites desorbs at 650 K (table 1).

It is quite interesting why these two kinds of adsorbed nitrogen, the N(l) and the N(h), have different reactivity with respect to H_2. There may be two reasons. The first one is due to the bond strength of metal–nitrogen, the second one relates to the catalytic activity of the adsorption sites.

5. Conclusion

Two kinds of adsorbed N atoms, N(l) and N(h), desorbing at 490 and 650 K, respectively, are accumulated on a $Pt_{0.25}Rh_{0.75}(100)$ surface by performing a reaction of NO+CO. On a Pt-enriched clean $Pt_{0.25}Rh_{0.75}(100)$ surface, the N(l) desorbing at 490 K is predominant, and the N atoms react with H_2 at 400 K. On the other hand, both the N(l) and the N(h) are accumulated on a p(3 × 1)-O or c(2 × 20)-O/$Pt_{0.25}Rh_{0.75}(100)$ surface, the former reacts with H_2 at 400 K, but the latter does not.

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