Catalytic Activity of Pt-Deposited Rh(110) Bimetallic Surface for NO + H₂ Reaction

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The Pt/Rh(110) bimetallic surface was prepared by electrochemical deposition of Pt ions on a Rh(110) surface. The Pt/Rh(110) surface was stable at 760 K in vacuum, but Rh atoms were extracted onto the Pt layer at 760 K by heating in O₂. The LEED pattern sequentially changed from $p(1 \times 1)$ with high background to a $p(1 \times 3)$ and a $c(2 \times 2)$ by heating in O₂. When the $c(2 \times 2)$ surface was heated at 760 K in H₂, the LEED pattern changed to $p(1 \times n)$. Extraction of the Rh atom occurred also during the NO + H₂ reaction, which was monitored by cyclic voltammograms. The $p(1 \times n)$ Pt/Rh(110) surface is highly active for the NO + H₂ reaction of the surface for the NO + H₂ reaction.

1. Introduction

Pt-Rh catalyst is known by the name of the three-way catalyst, which was developed for environmental protection from NO_x , hydrocarbon, and CO exhaust from automotive vehicles.¹ A real Pt-Rh catalyst is prepared by impregnation of Pt and Rh ions on Al₂O₃ or CeO₂-Al₂O₃² It is an interesting feature that a small amount of Rh is indispensable for getting prominent catalytic activity of the Pt-based catalyst for NO_x reduction or CO oxidation. For example, it was shown that a supported Pt/ Rh catalyst has a higher activity than a supported Pt and a supported Rh catalyst for the oxidation of CO in the presence of NO.³ Dispersion of Rh or Pt atoms is also important for the practical catalyst to get high catalytic activity. D'Aniello et al.⁴ demonstrated that the catalytic activity was recovered by redispersion of Pt or Rh atoms for an aged Pt-Rh by treating with Cl₂. So far, many efforts have been applied to get the Pt-Rh catalyst with higher activity and longer life. However, the role of Rh in the three-way catalyst is still not clear. To throw light on this subject, we precisely studied the structure and catalysis of the Pt/Rh(100) alloy surface and Rh-deposited Pt(100) and Pt-deposited Rh(100) bimetallic surfaces. It was shown that a Pt_{0.45}Rh_{0.55} alloy tip annealed at 973 K is composed of a Pt-enriched topmost layer and a Pt-depleted (Rh enriched) second layer.⁵ On the other hand, it was proved that when a Pt_{0.25}Rh_{0.75}(100) surface is annealed at higher than 950 K, the Pt fraction of the alloy surface is lowered with increasing annealing temperature and is almost equal to the Pt fraction of the bulk composition at 1300 K. From these results, we deduced that the alloy surface will be in equilibrium at higher than 950 K and that the equilibrium Pt fraction decreases with increasing annealing temperature. However, when a Pt-enriched Pt_{0.25}-Rh_{0.75}(100) surface is exposed to O₂ or NO, a clear $p(3 \times 1)$ LEED pattern appears with increasing Rh fraction on the surface even at 450 K.⁶ It was also shown that a similar $p(3 \times 1)$ structure is accomplished on a Rh-deposited Pt(100) surface⁸ when the surface is heated in O₂ or NO at 400 K. From these results, it was deduced that the $p(3 \times 1)$ pattern reflects the reconstructive growth of a common surface structure such as Rh-O/Pt-layer by the reaction of Rh atoms with oxygen. Furthermore, it was proved that when a Pt-deposited Rh(100) surface was heated in O₂ at 600 K, the Rh atom was extracted by reacting with oxygen and the LEED pattern changed to a

combined $p(3 \times 1) + p4g \ p(2 \times 2)$ structure. When this $p(3 \times 1)$ + $p4g p(2 \times 2)$ surface is exposed to H₂ at room temperature, the $p(3 \times 1) + p4g p(2 \times 2)$ pattern is readily changed to the (1×1) structure. When this $p(1 \times 1)$ surface is exposed to O₂, the $p(3 \times 1)$ pattern is recovered at room temperature. From these results, it was deduced that the $p(3 \times 1) + p4g p(2 \times 2)$ structure is attributable to an oxygen-induced reconstruction of Rh containing a (100)-like Pt-enriched layer. We studied the catalytic activity of Pt_{0.25}Rh_{0.75}(100), Rh/Pt(100),^{7,8} and Pt/Rh- $(100)^{8,9}$ surfaces for the NO + H₂ reaction as a model catalyst for the NO reduction. It is worthy of note that the real catalysis in the exhaust gas and the reaction of NO with H₂ on Pt_{0.25}-Rh_{0.75}(100), Rh/Pt(100), and Pt/Rh(100) surfaces work under entirely different circumstances; that is, the real catalyst works in the presence of hydrocarbons, NO_x, CO, SO_x, and particulates at rather high pressures.

Although the working conditions for the model catalyst and the real catalyst are largely different, the phenomena observed on the single-crystal surfaces may reflect the essential role of Rh. In our previous studies, it was shown that Rh/Pt(100), Pt/ Rh(100), and Pt-Rh(100) surfaces are activated by reconstruction; that is, a common $p(3 \times 1)$ surface is established on these three surfaces by O_2 or NO. Therefore, it is interesting whether other crystallographic planes are also activated by the reconstruction. From this point of view, the structure and the catalytic activity for NO + H_2 reaction were studied on the Pt/Rh(110) bimetallic surface that was prepared by electrochemical deposition of Pt ions on a $p(1 \times 1)$ clean Rh(110) surface. In our series of experiments, it will be shown that the voltammogram is a promising method for diagnosing the reconstructed surface because it is sensitive to the composition of the topmost layer of the working electrode. In this paper, the catalysis and surface structure of the Pt/Rh(110) surface were studied by combining the LEED and XPS analyses and the electrochemical method.¹⁰

2. Experimental Section

A clean Rh(110) surface was obtained by repeated Ar⁺ sputtering and annealing in ultrahigh vacuum (UHV) at 1300 K. After that, the Rh(110) disk was transferred into a small volume high-pressure cubic reactor attached to the main UHV chamber, and the cubic reactor was filled with 1 atm of highly pure Ar gas. After that, an electrochemical glass cell containing a solution of 0.05 M H₂SO₄ and 3.0×10^{-5} M PtCl₆²⁻ was lifted up into the cubic reactor so that the solution surface

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[®] Abstract published in Advance ACS Abstracts, January 1, 1997.



Figure 1. (a) Cyclic voltammogram of $p(1 \times 1)$ Rh(110) surface in 5 × 10⁻² M H₂SO₄. (b) Cyclic voltammogram of Pt-deposited Rh(110) surface in 5 × 10⁻² M H₂SO₄.

meniscus makes contact with one side of Rh disk as described in previous paper.^{7–9} Then the electrochemical deposition of Pt ions was carried out by applying cyclic voltammetry. After the deposition of a certain amount of Pt on the Rh(110) surface, the Rh disk was washed in the cubic reactor with pure water to avoid the effects of Cl⁻ ions,¹¹ and then the cyclic voltammogram of the Pt-deposited Rh(110) surface in a 0.05 M H₂SO₄ solution was recorded. After the electrochemical measurement in the H₂SO₄ solution, the Rh disk was pulled back to the UHV chamber for characterization by LEED and XPS. No detectable contamination was observed on the Pt-deposited Rh(110) surface, provided that we used ultrapure water and highly pure Ar gas.

Catalytic reduction of NO with H₂ was carried out in the cubic cell by raising the temperature of the Pt/Rh(110) crystal in a flow of a mixture of 5.8×10^{-9} Torr of NO and 1.6×10^{-8} Torr of H₂. The temperature-programmed reaction (TPR) of NO + H₂ was monitored by measuring N₂ with a quadrupole mass analyzer, where the crystal temperature was raised in a rate of 1 K/s.

3. Results and Discussion

A cyclic voltammogram of a clean Rh(110) surface in a 0.05 M H₂SO₄ solution is shown in Figure 1a. Sharp peaks at -0.24 and -0.21 V(SCE) are attributable to the hydrogen adsorption (H⁺ + e⁻ \rightarrow H(a)) and desorption (H(a) \rightarrow H⁺ + e⁻) processes. The charge for the hydrogen desorption peak at -0.21 V(SCE) in Figure 1a was about 161 mC cm⁻², which is almost equal to the calculated value of 157 mC cm⁻² for a flat Rh(110) surface by assuming one hydrogen atom for each Rh atom on the (1×1) Rh(100) surface. The obtained voltammogram (Figure 1a) is very similar in shape to that reported by Gómez et al.,¹² but peaks at -0.17 V(SCE) of their voltammogram are more sharp compared to the corresponding peaks at -0.21 V in our voltammogram, which may be reflected by the quality of the Rh(110) surface.



Figure 2. N₂/NO ratio in TPR on Rh(110) and Rh/Pt(110) surfaces.

prepared in the UHV system showed a clear $p(1 \times 1)$ LEED pattern, but the spots were a little diffuse.

It is worthy of note that the hydrogen adsorption/desorption peaks have almost equal potentials at the peak maximum on both Rh(110) and Rh(100) surfaces.¹³ It is quite a contrast to that on Pt(110) and Pt(100) surfaces, where the voltammogram on Pt(110) is entirely different from that on Pt(100) surface.^{14,15} This fact indicates that the redox reaction of hydrogen, H⁺ + $e^- \rightleftharpoons$ H, takes place at the same potential on (1×1) Rh(100) and (1×1) Rh(110) surfaces but not on the Pt surfaces.

When a Rh(110) surface was heated in a flow of 5.8×10^{-9} Torr of NO and 1.6×10^{-8} Torr of H₂, the N₂ pressure started to increase at ca. 360 K and made a peak at about 440 K and was followed by a continuous increase with a maximum at about 550 K as shown in Figure 2 with open circles. The N₂ peak appearing at 440 K is given by a desorption-mediated reaction of adsorbed NO, which is similar to that observed on the Rh-(110) surface.¹⁶ The catalytic reaction of NO with H₂ on Rh-(110) was brought about at 550 K, which is lower than the corresponding temperature of 600 K on Rh(100) surface.¹³ This result indicates that the NO + H₂ reaction on Rh(110) and Rh-(100) surfaces is also as structure sensitive as that on Pt(100) and Pt(110) surfaces,¹⁷ but it is not as remarkable compared to that on Pt(110) and Pt(100) surfaces. The as-deposited surface of ca. 1.5 monolayers of Pt ions on Rh(110) gave a XPS peak ratio of Rh $3d_{5/2}$ /Pt $4d_{3/2} = 1.1$, but this surface showed no LEED pattern. No appreciable contamination was detected on this surface by XPS. This reveals that the deposition of Pt on Rh(110) surface is not pseudomorphic.

It was shown that the XPS peak for the Pt of a Pt-deposited Rh(100) surface changes little by heating to 1050 K in UHV^{8,9} but is drastically changed by heating in O₂, and a $p(3\times1)$ LEED pattern is established at 600 K with increasing Rh atoms by reacting with oxygen.^{8,9} Recently, our STM image shows that the $p(3\times1)$ surface is reflected by an ordered arrangement of Pt and Rh–O rows on the surface.¹⁸ Therefore, hereafter the reconstructed surface is described by a (Pt–Rh–O–Pt). If we compare the catalytic activity of Rh(100), Pt/Rh(100), and (Pt–Rh–O–Pt)/Rh(100) for the reaction of NO + H₂, it is clear that the (Pt–Rh–O–Pt)/Rh(100) is extremely active for the NO + H₂ reaction.¹³ From these results, it was deduced that the reconstruction is responsible for the prominent catalytic activity of the Pt–Rh catalyst for the NO + H₂ reaction.

As mentioned above, the Pt layer on the Pt/Rh(100) surface is stable at ca. 1000 K in vacuum,8 but the XPS ratio of Rh $3d_{5/2}$ /Pt $4d_{3/2}$ for the Pt/Rh(110) surface was increased by annealing at 1000 K for 30 min. This fact indicates that the Pt atoms on the Rh(110) surface are less stable than those on the Rh(100) surface so that the Pt atoms are diffused into the Rh crystal. In other words, thermal stability of the Pt layer on the Rh surface depends on the crystallographic planes. A Pt/Rh-(110) surface annealed at 1000 K, which gave a $p(1 \times 1)$ LEED pattern, did not show a very high activity for the reduction of NO with H₂, as shown in Figure 2 with solid circles. It is interesting that a characteristic N2 peak observed on the Rh-(110) surface also appeared at ca. 440 K, as shown in Figure 2 with open circles, which may suggest that the Pt/Rh(110) annealed at 1000 K is almost covered with Rh atoms instead of Pt.

When an as-deposited Pt/Rh(110) surface was heated in 1 \times 10⁻⁷ Torr of H₂ at 760 K for 10 min, the LEED pattern changed to a $p(1 \times n)$ but the Rh $3d_{5/2}$ /Pt $4d_{3/2}$ ratio of the XPS peaks changed little. This $p(1 \times n)$ LEED pattern was stable at 760 K in UHV and no O 1s XPS peak was detected. When the $p(1 \times n)$ surface was annealed at 760 K in 1×10^{-7} Torr of O₂ for 60 min, the LEED pattern sequentially changed from the $p(1 \times n)$ to a $p(1 \times 3)$ pattern and finally to a $c(2 \times 2)$ pattern as shown in Figure 3. In accordance with the LEED pattern change, the Rh 3d_{5/2}/Pt 4d_{3/2} ratio and the O 1s peak of the XPS spectrum increased concomitantly as shown in Figures 3 and 4. Taking account of the fact that the Pt and Rh atoms cannot diffuse very rapidly at temperatures lower than 900 K,19 the rapid increase of the Rh 3d_{5/2}/Pt 4d_{3/2} ratio at 760 K is caused by the reaction of Rh with O₂. The $p(1 \times n)$ and the $p(1 \times 3)$ patterns were stable even at 760 K in H₂, but the $c(2 \times 2)$ surface changed to a $(1 \times n)$ structure in 1×10^{-7} Torr of H₂ at 760 K. It should be pointed out that the $c(2 \times 2)$ is not influenced at room temperature by exposure to H_2 . Contrary to the Pt/Rh(110) surface, the Pt/ Rh(100) surface gives the $p(3 \times 1) + p4g p(2 \times 2)$ LEED pattern by heating in O₂ at 600 K and this surface readily changes to the $p(1 \times 1)$ structure at room temperature by exposure to H₂.

As mentioned above, Pt layer formed on the Rh surface has different stability depending on the crystallographic planes of Rh crystal in vacuum. However, the extraction of Rh by O_2 was commonly observed on both the Pt/Rh(110) and Pt/Rh-(100) surfaces. The Pt/Rh(100) surface gave high catalytic activity for the NO reduction when Rh atoms are extracted by reacting with O_2 ; that is, the $p(3 \times 1)$ (Pt-Rh-O-Pt)/Rh(100)



Figure 3. Change of the Rh $3d_{5/2}$ /Pt $4d_{3/2}$ ratio of the XPS spectrum and LEED pattern of Pt/Rh(110) surfaces.

structure is established. To compare the catalytic activity of the Pt/Rh(110) surface, the reaction of NO with H₂ was performed on a $p(1 \times n)$ Pt/Rh(110) surface having a ratio of Rh 3d_{5/2}/Pt 4d_{3/2} = 2.7, where the $p(1 \times n)$ surface was previously prepared by heating the $c(2 \times 2)$ surface in 1×10^{-7} Torr of H₂ at 760 K. As mentioned above, the Rh/Pt ratio of the $p(1 \times n)$ Pt/Rh(110) surface was changed little by treating with H₂ at 760 K, and it is the same on the $c(2 \times 2)$ surface obtained by heating in O₂. However, as shown in Figure 2 with triangles, the $p(1 \times n)$ Pt/Rh(110) surface showed a remarkable catalytic activity for the reaction and N₂ evolution occurred at ca. 400 K, which is almost the same temperature for the NO + H₂ reaction on the $p(3 \times 1)$ (Rh–O–Pt)/Rh(100) surface.¹² This fact may reveal that similar active sites are formed on both (Rh– O–Pt)/Rh(100) and $c(2 \times 2)$ or $p(1 \times n)$ Pt/Rh(110) surfaces.

By reaction of Rh atoms with O, Rh atoms were segregated on the $Pt_{0.25}Rh_{0.75}(100)$ alloy surface by exposure to O_2 or NO,²⁰ and it is the same on the Pt/Rh(110) surface. The extraction of Rh atoms on the Pt/Rh(110) surface by reacting with O_2 can be diagnosed by the cyclic voltammogram for the Pt/Rh(110) surface. To avoid the influence of Cl⁻ ions from PtCl₆²⁻ on the voltammogram,¹¹ the Pt/Rh(110) disk was washed with superpure water and then the cyclic voltammogram was obtained in 0.05 M H_2SO_4 solution. It is known that the peak at -0.21V(SCE) attributable to the Rh(110) surface (Figure 1a) is suppressed as the deposition of Pt atoms increases and a shoulder appears at around -0.15 V(SCE), as shown in Figure 1b. After the washing of this surface with superpure water, the Pt/Rh-(110) disk was transferred to the main UHV chamber and was characterized by LEED and XPS. The amount of Pt deposited on the Rh(110) surface was estimated to be 0.9 monolayer by the XPS, where no clear LEED pattern was observed.

Although this Pt/Rh(110) surface was heated at a rate of 1 K/s to 760 K in UHV, no clear LEED pattern was observed. The Rh $3d_{5/2}$ /Pt $4d_{3/2}$ ratio is not very sensitive to the compositional change of the topmost layer,²¹ but the cyclic voltammogram may be sensitive to the topmost layer. In fact, the cyclic voltammogram for the surface annealed at 760 K in UHV gave a new peak at ca. -0.15 V(SCE) as shown in Figure 5a, although the ratio of Rh/Pt changed little. By comparison of the cyclic voltammogram of the annealed surface to that of Rh(110) surface, the new peak at -0.15 V(SCE) is responsible for the characteristic peak of the Pt layer. Therefore, the Pt



Figure 4. Change of the O 1s peak of the XPS spectrum of Pt/Rh-(110) surfaces: (i) Rh/Pt = 1.3; (ii) Rh/Pt = 1.8; (iii) Rh/Pt = 2.5.



Figure 5. (a) Cyclic voltammogram of Pt/Rh(110) surface ($\theta_{Pt} = 0.9$) heated to 760 K in 5 × 10⁻² M H₂SO₄, where the Pt/Rh(110) was annealed at 760 K in vacuum. (b) Cyclic voltammogram of Pt/Rh(110) surface ($\theta_{Pt} = 0.9$) in 5 × 10⁻² M H₂SO₄ after the TPR experiment in a flow of NO and H₂ to 760 K.

atoms might arrange themselves in an array over the surface by annealing.

The Pt/Rh(110) surface was subjected to the TPR of NO + H_2 by raising the temperature at a rate of 1 K/s. The Rh $3d_{5/2}$ Pt 4d_{3/2} ratio changed little during the TPR, but a new peak appeared in the voltammogram at -0.22 V(SCE) as shown in Figure 5b, which indicates the segregation of Rh atoms during TPR; that is, the cyclic voltammetry sensitively proves the segregation of Rh atoms on the topmost layer during the NO + H₂. From these results, we can conclude that a chemical reconstruction of the Pt/Rh(110) surface may be responsible for the activation of the Pt/Rh(110) catalyst, and (Pt-Rh-O-Pt) constitution might be formed on these surfaces by reacting with O_2 or NO, which is the active surface for the reaction of NO + H₂. Considering the chemical activation forming a specific constitution observed on Pt_{0.25}Rh_{0.75}(100), Rh/Pt(100), Pt/Rh-(100), and Pt/Rh(110) surfaces, a similar activation could be expected on the Pt-Rh/washcoat catalyst.

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