The role of Rh on Pt-based catalysts: structure sensitive NO + H_2 reaction on Pt(110) and Pt(100) and structure insensitive reaction on Rh/Pt(110) and Rh/Pt(100)

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The catalytic activity of the Pt(110) surface for the reaction of NO + H_2 was much less than that of the Pt(100) surface. However, the catalytic activity of the Rh deposited Pt(110) surface was almost equal to that of the Rh deposited Pt(100) surface. That is, the catalytic reaction of NO + H_2 on Pt(110) and Pt(100) surfaces is highly structure sensitive, but it changes to structure insensitive by the deposition of Rh atoms. These results are rationalized by formation of an active overlayer on the Pt(110) and Pt(100) surfaces, which is very analogous to the Rh–O/Pt-layer formed on Rh/Pt(100), Pt/Rh(100) and Pt–Rh(100) alloy surfaces during catalysis. The formation of the common overlayer of Rh–O/Pt-layer during catalysis is responsible for the structure insensitive catalysis of Rh deposited Pt-based catalysts, which is an important role of Rh in a three way catalyst.

Keywords: Pt(110); Pt(100); Rh/Pt(110); Rh/Pt(100); activity; structure sensitivity

1. Introduction

Somorjai [1] showed that some catalytic reactions depend strongly on the surface geometry such as surface defects and/or the crystallographic planes. On the other hand, some reactions are known to be structure insensitive [2]. Therefore, catalytic reactions have been classified into structure sensitive and insensitive reactions. Structure sensitive catalysis has been rationalized as reactions caused by specific sites, but structure insensitive catalysis is in most cases inadequately understood [3].

The Pt–Rh catalyst is known as the three way catalyst for environmental protection from NO_x in automotive exhaust gas. It is interesting that a small amount of

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Rh is an indispensable component of the Pt-based catalysts for NO_x reduction, but the role of Rh is still controversial. In order to throw light on the role of Rh, we studied the adsorption and catalysis on a $Pt_{0.25}Rh_{0.75}(100)$ alloy surface [4,5], Rh deposited Pt(100) [6] and Pt deposited Rh(100) surfaces [7]. From a series of experiments on the alloy surface, it was deduced that the top two layers of the Pt–Rh alloy surface undergo chemical restructuring above 400 K by NO and/or O_2. As a result, a common hybrid overlayer of Rh–O/Pt-layer is built up on the alloy surface. It was shown that the same overlayer structure is established on the Pt deposited Rh(100) surface as well as on the Rh deposited Pt(100) surface. That is, the Pt–Rh(100) alloy surface exposed to O_2 or NO gives a clear p(3 × 1) LEED pattern at around 400 K, which may reflect the formation of such a hybrid overlayer as the Rh–O/Pt-layer on the alloy. To confirm the p(3 × 1) pattern for the Rh–O/Pt-layer, a Rh deposited Pt(100) surface was prepared by electrochemical deposition of Rh ions. It was confirmed that the Rh/Pt(100) surface gives a very sharp p(3 × 1) LEED pattern by heating in NO or O_2 which is the same pattern as observed on the Pt–Rh(100) alloy surface [6]. Therefore, it was concluded that the p(3 × 1) pattern of the Pt–Rh(100) alloy surface indicates the formation of the Rh–O/Pt-layer by chemical restructuring.

In this paper, the catalytic reaction of NO + H_2 was studied on Rh/Pt(110) and Rh/Pt(100) surfaces, where the Rh/Pt(110) was prepared by the electrochemical deposition of Rh ions on a clean p(1 × 2) Pt(110) surface. The results make clear the important roles of Rh atoms for the Pt-based three way catalyst.

2. Experimental

A clean p(1 × 2) missing row Pt(110) surface was obtained by Ar sputtering, oxidation with 1×10^{-7} Torr of O_2 at 770 K, and annealing in UHV at 1100 K. A clean Pt(110) surface with a p(1 × 2) missing row structure was transferred into a small volume of high pressure cubic reactor attached to the main UHV chamber. The high pressure reactor was filled with Ar of 1 atm pressure. Then, an electrochemical glass cell containing a solution of 0.05 M $H_2SO_4 + 4.6 \times 10^{-4}$ M $RhCl_3$ was lifted up into the reactor to make meniscus contact with one side of the Pt(110) disk. In the present experiment, Rh was deposited as more than one monolayer on the p(1 × 2) Pt(110) surface, which gave no LEED pattern. When the excess Rh deposited on the Pt(110) surface was removed by Ar ion sputtering and annealing in 1×10^{-7} Torr of O_2 at 770 K, a c(2 × 2) LEED pattern appeared at first, and then it changed to a clear p(1 × 2) pattern by repeated Ar ion sputtering and subsequent annealing in vacuum. The final amount of Rh on the p(1 × 2) surface was estimated to be less than one monolayer, where the amount of Rh was evaluated by the relative intensity of the AES signals for Pt and Rh.

3. Results and discussion

When the Pt(100) surface was exposed to a flow of 5.8×10^{-9} Torr of NO and 1.6×10^{-8} Torr of H_2 and then heated up at a rate of 0.9 K/s, a sharp N_2 peak (indicated by N_2/NO) appeared at about 460 K and a broad N_2 formation curve (open circle) was followed as shown in fig. 1. The sharp N_2 peak at 460 K corresponds to the autocatalytic decomposition of NO [8] or the explosive reaction of NO [9]. The following broad curve of N_2 is caused by the catalytic reduction of NO with H_2 on the Pt(100) surface. When the NO + H_2 reaction was performed on a Rh deposited Pt(100) surface, however, a different TPR curve (solid circle) was obtained as shown in fig. 1. That is, the N_2 spike peak at about 460 K reflecting the explosive reaction disappeared and the catalytic reaction giving N_2 is markedly enhanced.

On the other hand, the TPR of NO with N_2 on the Pt(110) surface (open circle) in fig. 2 is apparently less active compared to that on the Pt(100) surface (fig. 1). In other words, we can say that the catalytic reaction of NO + H_2 on Pt(100) and Pt(110) surfaces is structure sensitive.

The Pt(110) surface is undoubtedly much less active for the NO + H_2 reaction. However, the Rh deposited Pt(110) surface showed a remarkable catalytic activity for the NO + H_2 reaction (solid circle) as shown in fig. 2, that is, the Pt(110) surface is dramatically activated by depositing Rh. Furthermore, the activity of the Rh/Pt(110) surface for the reaction of NO + H_2 (solid circle) is very close to that of the Pt–Rh(100) alloy surface (cross) as indicated in fig. 2. This fact implies that the structure sensitive catalysis of the Pt surfaces for the reaction of NO + H_2 changes to the structure insensitive catalysis by the Rh deposition.

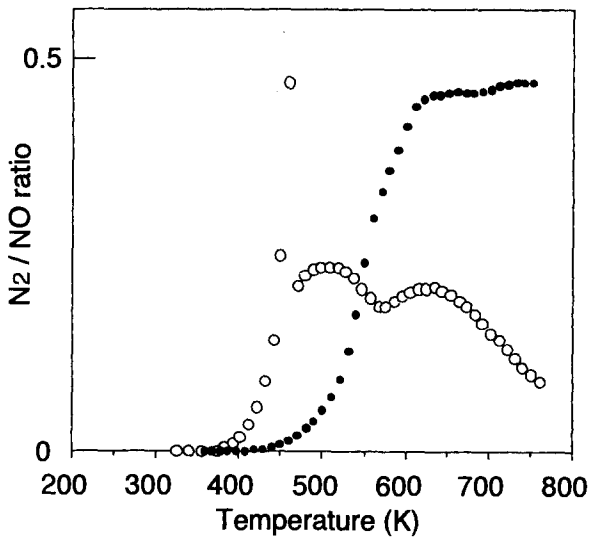

Fig. 1. N_2/NO ratio in the temperature programmed reaction (TPR) of NO + H_2 on Pt(100) (○) and Rh/Pt(100) surfaces (●), where the Rh was equivalent to ca. 1.6 monolayer. NO = 5.8×10^{-9} Torr, H_2 = 1.6×10^{-8} Torr, and rise in temperature was 0.9 K/s.

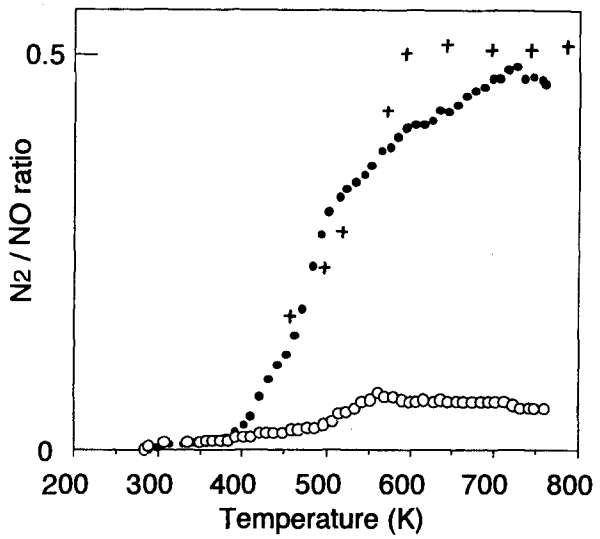

Fig. 2. N_2/NO ratio in the TPR of NO + H_2 on Pt(110) (○) and Rh/Pt(110) surfaces (●), where the Rh was equivalent to ca. 1.5 monolayer. TPR on $Pt_{0.25}Rh_{0.75}$(100) surface (+) was plotted as a reference. NO = 5.8×10^{-8} Torr, H_2 = 1.6×10^{-8} Torr.

Furthermore, as shown in fig. 3, the catalytic activity of the Rh/Pt(110) surfaces is independent of the Rh content, where the amount of Rh was lowered by Ar ion sputtering and subsequent annealing. A more surprising fact was that the catalytic activity of the Rh/Pt(110) surface is little influenced by surface roughening, that

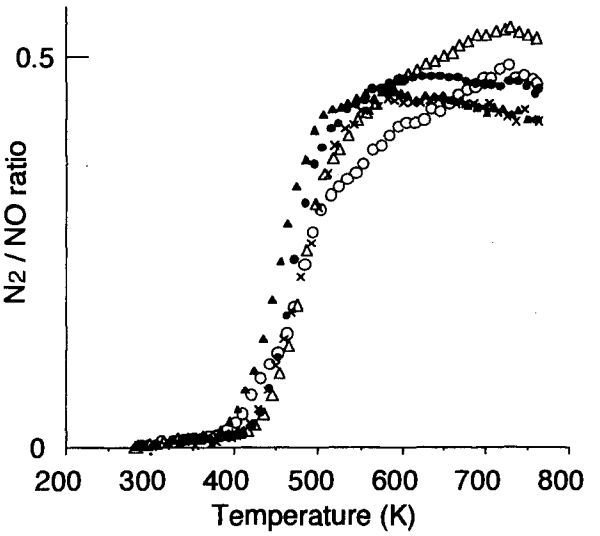

Fig. 3. N_2/NO ratio in the TPR of NO + H_2 on Rh/Pt(110) surface with different Rh contents. Amount of Rh in monolayer unit: 1.5 (○), 1.0 (△), 0.61 (●), 0.53 (▲), 0.37 (×). NO = 5.8×10^{-9} Torr, H_2 = 1.6×10^{-8} Torr.

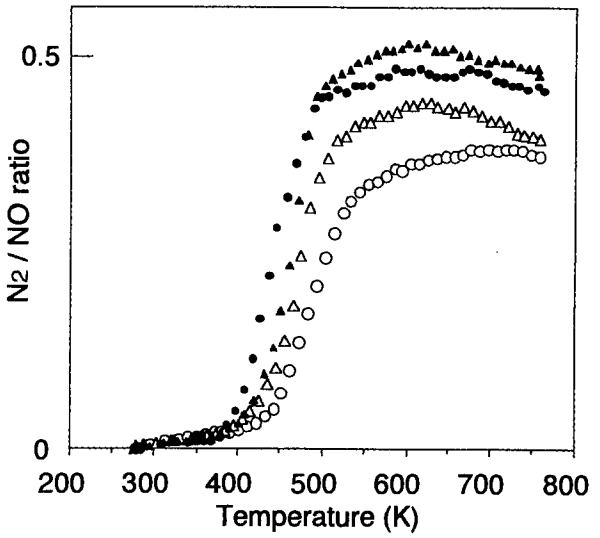

Fig. 4. Activity of the rough Rh/Pt(110) surfaces (○, △) sputtered with Ar and the smoothed Rh/Pt(110) surfaces by annealing (●, ▲). Amount of Rh: 0.69 (○, ●) and 0.43 (△, ▲). NO $= 5.8 \times 10^{-9}$ Torr, $H_2 = 1.6 \times 10^{-8}$ Torr.

is, the activity of the sputtered surface is not so different from the annealed surface as shown in fig. 4. It should be pointed out that the catalytic activity of the Rh/Pt(110) surface for the reaction of NO with H_2 is similar to that of $Pt_{0.25}Rh_{0.75}(100)$ alloy surfaces as shown in fig. 2. Based on these results, we can conclude that Rh atoms activate the Pt surfaces for the reaction of NO with H_2, and the structure sensitive catalysis for the NO with H_2 reaction changes to the structure insensitive catalysis. In our previous paper [7], it was shown that the Rh/Pt(100), Pt/Rh(100) and $Pt_{0.25}Rh_{0.75}(100)$ alloy surfaces during the catalysis are covered with a common overlayer of Rh–O/Pt-layer [7].

Taking these facts into account, it may be deduced that the Rh/Pt(110) surface is also covered with a similar Rh–O/Pt-layer during the catalysis, that is, the Rh activates the Pt surfaces by making an active overlayer of Rh–O/Pt-layer structure, which is responsible for the prominent catalytic property of the Pt–Rh three way catalyst.

As was mentioned above, structure insensitive catalysis is in most cases inadequately understood. For this reason, the role of Rh deduced in this paper is suggestive, which reminds us of a similar structure insensitive catalysis of the methanation reaction on Ni surfaces, where the nickel surfaces, Ni(100), Ni(110) and Ni(111), are covered with a common surface carbide [3].

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