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# ENHANCING AND IMPROVING EFFECTS OF Sn ON Ru-$Al_2O_3$ CATALYST ON THE REDUCTION OF NO AND CO IN THE OXIDATIVE ATMOSPHERE

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The catalytic activity of Ru-γ-$Al_2O_3$ on simultaneous removal of NO and CO in oxidative atmosphere was enhanced by alloying with Sn. The degree of the enhancement was lesser than that observed on Rh-Sn-γ-$Al_2O_3$. The weight loss caused by the evaporation of toxic higher oxides of Ru from the catalyst was lowered by alloying with Sn.

Ruthenium is an active metallic component in the catalyst for automotive pollution control, but Ru is known to show low activity in the presence of $O_2$.[1] The evaporation of toxic $RuO_4$ from catalyst at ca. 373 K is an additional shortcomming of Ru in practical applications.[2]

The experimental methods were similar to those described before.[3] The concentration of Ru was 0.5 wt %. Tin-containing catalysts were prepared by adding Sn to the above amount of Sn to obtain the catalyst of known Ru/Sn atomic ratio. E.Merck's γ-$Al_2O_3$ was used as the catalyst support. This γ-$Al_2O_3$ was immersed in a solution containing a known concentration of $RuCl_3$ and $SnCl_2,2H_2O$. After evaporation and drying, the catalyst was decomposed and reduced in a flow of $H_2$ at 578 K for 8 h at normal pressure. The catalyst was 60 to 100 mesh in size. The catalyst was treated at 353 K for 0.5 h in $2.7 \times 10^4$Pa of $O_2$ and reduced at 673 K for 1 h in $2.7 \times 10^4$Pa of $H_2$ in the reactor just before reaction experiments. The catalyst was evacuated to $10^{-3}$Pa before introducing the reactant gas. The reactant gas was two kinds: the first kind was made up of one part of NO, one part of CO, and y parts of $H_2$ ($y = 0$ to 1.0), and the second was made up of one part of NO, and one part of CO, and x parts of $O_2$ ($x = 0$ to 0.8). These gases are expressed in the following as NO + CO + $yH_2$ and NO + CO + $xO_2$, respectively.

The evaporation of $RuO_4$ was followed by the decrease of the weight of metallic powders. The metallic powders were Ru powder and Ru-Sn (Ru/Sn = 3) alloy powder. The weight-loss was followed by using a Shimadzu MTB-50 micro-thermal balance, which can detect the weight-change of 1/200 mg. The samples were prepared by the decomposition and reduction of $RuCl_3$ and of the mixture of $RuCl_3$ and $SnCl_2,2H_2O$ in a flow of $H_2$ at 873 K for ca. 8 h under normal pressure. A known amount of this sample was reduced in a flow of $H_2$ at 773 K for ca. 3 h under normal pressure in the micro-thermal balance in advance. The subsequent procedures will be obvious in Figure 3.

Above 573 K, observed products were $N_2$, $CO_2$, $NH_3$, and a negligible amount of $N_2O$

Table 1 Deactivation and Recovery of Activity

| Catalyst | Reaction Temp.(K) | Conversion (%) of NO A | B | C | D |
|---|---|---|---|---|---|
| Ru | 548 | 99.9 | 14.5 | 21.4 | 99.9 |
| Ru/Sn = 1 | 573 | 99.9 | 23.0 | 31.3 | 99.9 |

Reaction conditions: $2.7 \times 10^4$ Pa, 420 s, x = y = 0

A: Results on fresh catalyst

B: Results on the evacuated catalyst used in A

C: Results on the reduced catalyst used in B, reduced at 673 K in $H_2$ for 1 h and evacuated

D: Results on the oxidized-and-reduced catalyst used in C, oxidized at 373 K in $O_2$ for 0.5 h and 673 K in $H_2$ for 1 h, and evacuated

in the case of $H_2$-containing atmosphere, and $N_2$, $CO_2$, and a negligible amount of $N_2O$ in the case of $O_2$-containing atmosphere. Deactivation of catalyst was observed in the repeated reaction experiments, and the activity was recovered by the oxidation-and-reduction treatment as shown in Table 1 (D). The results shown below were obtained by first 420 seconds of every reaction experiment on re-activated catalyst.

Table 2 shows results of the reaction between NO and CO. Nitrous oxide was observed in the case of low selectivity of $N_2$. The activity was lowered significantly at low temperature by alloying with Sn.

Figure 1 shows the activity of present catalysts under reductive and oxidative atmosphere. High conversion of NO and CO is observed in the $H_2$-containing atmosphere, but the conversion of CO decreased with increasing $H_2$-concentration. The selectivity of $NH_3$ was low but increased a little with increasing $H_2$-concentration. High conversion of CO was observed in the whole observed range in $O_2$-concentration as shown in Figure 1. The conversion of NO was higher on the catalyst of Ru/Sn = 3 than on Ru as shown in Figure 1. This observation will be shown in detail in Figure 2. The conversion of NO increased by alloying with Sn in the $O_2$-containing atmosphere. The promoting effect of Sn in oxidative atmosphere is lower on present catalyst than that on Ru-Sn-$\gamma$-$Al_2O_3$.[3] This may be ascribed to the difference among

Table 2 The Reaction between NO and CO

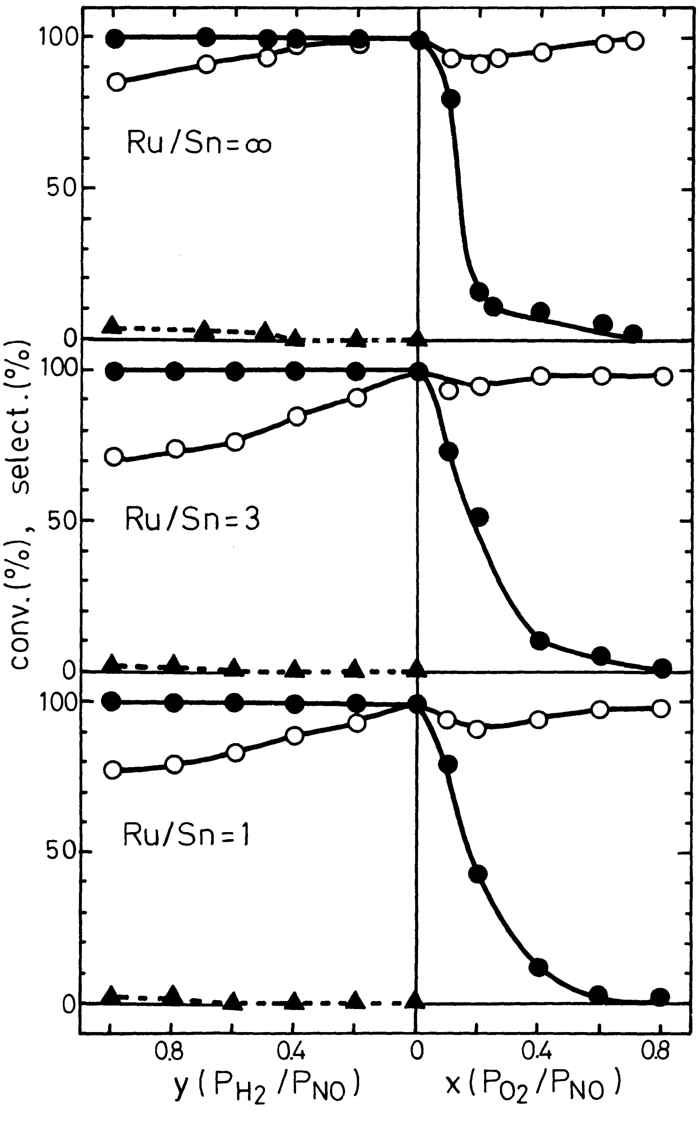
| Catalyst | Reaction Temp.(K) | Conv.(%) NO[a] | CO[b] | Selectivity of $N_2$ (%)[c] |
|---|---|---|---|---|
| Ru | 473 | 5.3 | 5.0 | 0.0 |
| | 523 | 14.8 | 11.0 | 44.5 |
| | 548 | 99.9 | 99.9 | 100 |
| Ru/Sn = 3 | 498 | 7.8 | 7.9 | 5.5 |
| | 548 | 19.9 | 18.9 | 35.4 |
| | 573 | 99.8 | 99.9 | 100 |
| Ru/Sn = 1 | 498 | 5.9 | 5.9 | 3.2 |
| | 548 | 18.0 | 17.5 | 20.5 |
| | 573 | 99.7 | 99.9 | 100 |

Reaction conditions: 420 s, $2.7 \times 10^4$ Pa, x = y = 0

a: $100 \times (N_2 + N_2O + 0.5NH_3)/(0.5NO + N_2 + N_2O + 0.5NH_3)$

b: $100 \times CO_2/(CO + CO_2)$, d: $100 \times N_2/(N_2 + N_2O + 0.5NH_3)$

the affinity of Ru, Rh, and Sn to oxygen. The values of first ionization potential are 7.7 eV for Rh, 7.5 eV for Ru, and 7.32 eV for Sn.[4] Accordingly, affinity for oxygen may increase in the following order: Rh < Ru < Sn. Ruthenium seems to hold adsorbed oxygen tightly in comparison with Rh. The spill over of adsorbed oxygen, from Rh to Sn suggested previously,[3] seems to proceed to a lesser extent on present catalysts than on Rh-Sn. In other words, surface Ru adsorbs oxygen so strongly that adsorbed oxygen cannot travel from Ru to Sn. The active site on Ru is hardly recovered. This will bring about the weak promoting effect of Sn in oxidative atmosphere in present catalysts.



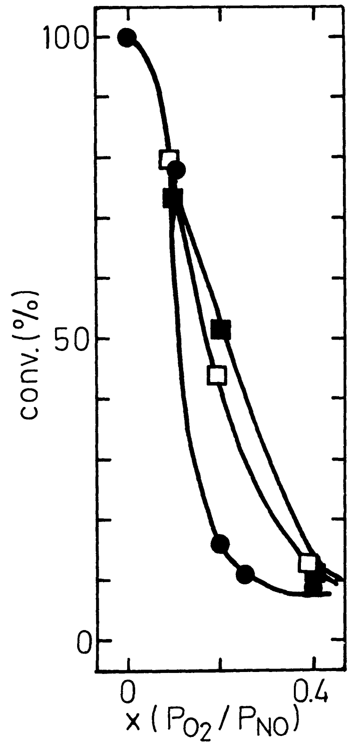


Figure 2, Details of Figure 1 in the low range of x

Ru ——●——

Ru/Sn = 3 ——■——

Ru/Sn = 1 ——□——

Figure 1, Effect of $H_2$ and $O_2$ concentration and of alloying with Sn on the efficiency of catalysts, NO + CO + y$H_2$ and NO + CO + x$O_2$

Reaction conditions: 573 K, (2.1 to 2.6) x $10^4$Pa, 420 s

——●—— conv. of NO

——○—— conv. of CO

- - -▲- - - selectivity of $NH_3$ (100 x 0.5$NH_3$)/($N_2$ + $N_2O$ + 0.5$NH_3$)

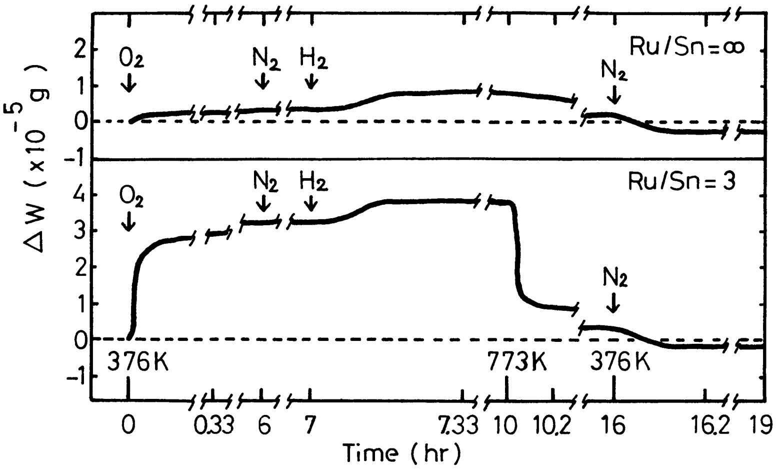


Figure 3, Time-course of the variation of the weight of the Ru and Ru-Sn at 376 K

Figure 3 shows the time-course of the variation of the weight of the Ru- and Ru-Sn-powder followed by micro-thermal balance. Table 3 shows the loss of the weight of samples by oxidation. The weight-loss per gram of Ru decreased from 0.154 % to 0.092 % by alloying with Sn.

Table 3 Decrease in the weight of the Ru- and Ru-Sn-powder by oxidation calculated from Figure 3

| | Ru | Ru-Sn |
|---|---|---|
| weight of powder used (mg) | 20.8 | 20.6 |
| decrease in the weight (mg) | $3.2 \times 10^{-2}$ | $1.3 \times 10^{-2}$ |
| decrease in the weight/g-sample (%) | 0.154 | 0.066 |
| decrease in the weight/g-Ru (%) | 0.154 | 0.092 |

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