CHEMISTRY LETTERS, pp.503-506, 1979. Published by the Chemical Society of Japan

OPTIMUM COMPOSITIONS OF Rh-Sn-γ-Al_2O_3 CATALYSTS FOR SIMULTANEOUS REDUCTION OF NITRIC OXIDE AND CARBON MONOXIDE

Mitsuo MASAI, Keisuke NAKAHARA, and Masakazu YABASHI
Department of Chemical Engineering, Faculty of Engineering, Kobe University, Rokkodai-cho, Nada-ku, Kobe 657

The simultaneous reduction of NO and CO on Rh-Sn-γ-Al_2O_3 was studied in reductive and oxidative atmosphere. The effect of alloying with Sn on catalytic activity was obviously observed in oxidative atmosphere. The reaction temperature lowered in the presence of O_2. The optimum Rh/Sn atomic ratio decreased with increasing concentration of O_2 in the reactant.

Rh-γ-Al_2O_3 catalyst is known to be an active three way conversion catalyst, i.e., for simultaneous reduction of nitrogen oxides, carbon monoxide, and hydrocarbons in automotive exhaust gas,[1] and the catalyst is very efficient in the narrow range of air-to-fuel ratio, 14.7 ± 0.1.[2] An oxidative reactant is fed to the catalyst at high air-to-fuel ratio, and a reductive reactant at low air-to-fuel ratio. Apart from practical problems, the narrow range of air-to-fuel ratio involves complicated but interesting problems. Conversion of NO to N_2 and of CO to CO_2 is to be expected, but actually N_2O and NH_3 are also observed.[1] Besides the main reaction (NO to N_2 and CO to CO_2), many auxiliary reactions must proceed at high reaction rates on single catalyst bed. We studied basically the possibility of widening the optimum range of air-to-fuel ratio.

Catalysts were prepared by impregnation method. The concentration of Rh was 0.5 weight percent. Tin-containing catalysts were prepared by adding Sn to the above amount of Rh to obtain the catalyst of known Rh/Sn atomic ratio. E. Merk'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 $Rh(NO_3)_3$ and $SnCl_2$. After evaporation and drying, the catalyst was calcined in a flow of air, and was then reduced in a flow of H_2, both at 773 K for 5 h at normal pressure. The catalyst was reduced again by H_2 at 773 K for 1 h in the reactor just before reaction experiments. The catalyst was evacuated to 10^{-3}Pa before introducing the reactant gas. The reactor was a conventional circulating system made of pyerx glass and contained 100 mg of catalyst. The reactant gases were two kinds: the first kind was made up of one part of NO, one part of CO, and a half part of H_2, and the second was made up of one part of NO, one part of CO, and x parts of O_2 ($x = 0$ to 0.63). These gases are expressed in the following as $NO + CO + 0.5H_2$ and $NO + CO + xO_2$ ($x = 0$ to 0.63). The details of conditions are shown in the correponding tables and Figure 1. The reaction gas was analyzed by using a

Table 1. Effect of alloying with Sn on catalytic activity[a] $NO + CO + 0.5H_2$.

Catalyst on γ-Al_2O_3	Conversion (%)		Selectivity (%)		
	NO	CO	N_2[b]	N_2O[c]	NH_3[d]
Rh	99	72	99	0	0.7
Rh/Sn = 1	99	85	98	0	2.1

a: 573 K, 2.7×10^4 Pa, 420 s
b: $N_2/(N_2 + N_2O + 0.5NH_3)$, c: $N_2O/(N_2 + N_2O + 0.5NH_3)$
d: $0.5NH_3/(N_2 + N_2O + 0.5NH_3)$

Hitachi RMU-6E mass spectrometer. The nitric oxide used for experiment was obtained from Matheson Gas Products. The carbon monoxide was obtained from Seitetsu Kagaku Kogyo K. K., Osaka, and the other gases were obtained commercially. The reagents were of G. R. grade.

Observed products were N_2, CO_2, NH_3, and a negligible amount of N_2O in the case of H_2-containing reactant, and N_2, CO_2, and a negligible amount of N_2O in the case of $NO + CO + xO_2$. Deactivation of the catalyst was observed in repeated reaction experiments but the activity was recovered by oxidation and reduction. The results shown below were obtained by the first 420 seconds of every reaction experiment on re-activated catalyst. As Table 1 shows, conversion of CO increased but the selectivity of NH_3 increased a little by alloying with Sn. Table 2 shows results obtained from the equimolar reactant mixture composed of NO + CO, where the selectivity of N_2 was almost 100 %. The activity decreased significantly at low temperatures by alloying with Sn (see Table 2). Apart from these results, a promoting effect of O_2 on the reaction was observed as shown in

Table 2. Effect of alloying with Sn on catalytic activity[a] NO + CO.

Catalyst on γ-Al_2O_3	Reaction temperature (K)	Conversion (%)	
		NO	CO
Rh	523	8.9	4.8
	548	96.7	80.9
	573	94.1	77.4
Rh/Sn = 1	548	13.4	11.3
	573	98.9	84.9

a: 2.1×10^4 Pa, 420 s

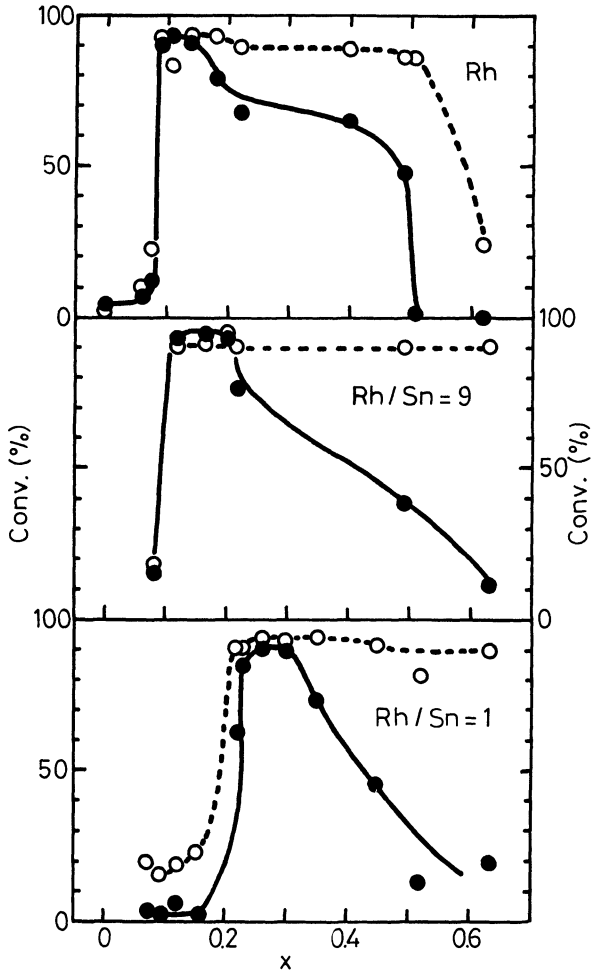

Figure 1, Effect of O_2 concentration and of alloying with Sn on the efficiency of catalysts
$NO + CO + xO_2$
473 K, (2.1 to 2.6) x 10^4Pa, 420 s
—●— conversion of NO
---○--- conversion of CO
$x = P_{O_2}/P_{NO}$

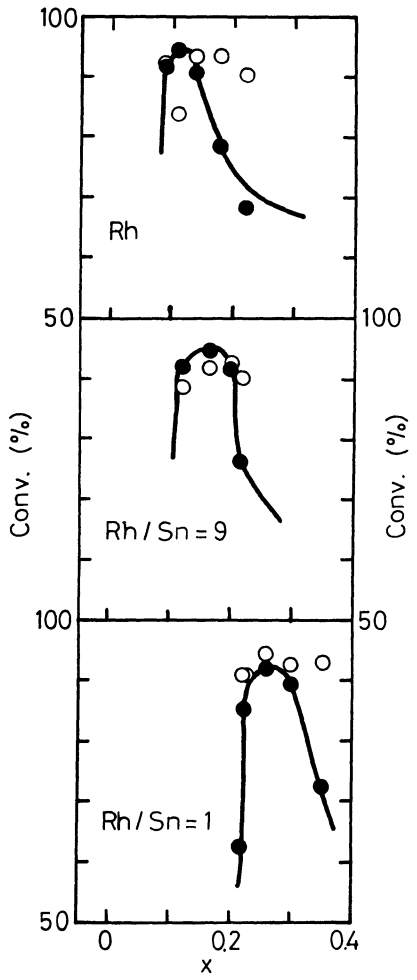

Figure 2, Details of Figure 1 in the neighbor of the maximum conversion of NO

Figure 1. The reaction proceeded even at 473 K, lower than the temperatures shown in Tables 1 and 2, in the presence of O_2. It is noticeable that the conversion vs. O_2 concentration curve has a maximum especially in the case of NO, and that the value of O_2 concentration corresponding to a maximum conversion of NO shifted to higher values with increasing Sn content of catalyst. The width of NO-conversion peak became wide on Sn-containing catalyst in comparison to that on Rh-γ-Al_2O_3. These effects will be shown in detail in Figure 2. A high degree of conversion of CO is maintained in the range where the degree of conversion of NO is high. The conversion of CO decreased sharply at high concentration of O_2

on Rh.

The lower reaction temperature in the presence of O_2 appear to result from the decomposition of adsorbed isocyanate (-CNO) which is the poison in this reaction on supported Cu catalyst,[3] and on Pt-Al_2O_3.[4] Adsorbed -CNO on Rh-Al_2O_3 has been reported.[5] Accordingly, decomposition of adsorbed -CNO by oxidation must be a reason that the reaction proceeded at low temperature, because the used catalyst was re-activated by oxidation and reduction. With the consideration that Sn is more likely to be oxidized than Rh, there may be another reason for Sn-containing catalysts. Adsorbed oxygen atom is reported to retard the decomposition of NO.[6] The adsorbed oxygen atom on Rh may travel from Rh to Sn probably by spill over and stay there. This will recover the active site on Rh. The adsorbed oxygen atom seems to be formed by the decomposition of NO and by the adsorption of O_2. This will explain the sharp decrease in the conversion of CO at high O_2 concentrations on Rh shown in Figure 1. Higher amount of Sn will be needed for higher O_2 concentrations to keep the activity high. This effect may lead to the shift of the O_2 concentration corresponding to the maximum efficiency with increasing O_2 concentration shown in Figure 1. The adsorbed oxygen atom on Sn will be removed by further reaction with a reducing agent such as CO.

It may be possible to make the narrow range of air-to-fuel ratio wide by using a catalyst bed which consists of the catalysts with several Rh/Sn ratios.

The support of this work by research grants from the Ministry of Education is hereby acknowledged. We appreciate the cooperation of Engineer Kenji NOMURA in carrying out the experiments.

REFERENCES

1. J. C. Schlatter and K. C. Taylor, J. Catal., 49, 42 (1977).
2. J. Wei, "Advances in Catalysis", Vol. 24 (ed. by D. D. Eley, H. Pines, and P. B. Weisz), pp.57 ~ 171, Academic Press, New York, 1975.
3. R. T. Rewick and H. Wise, J. Catal., 40, 301 (1975).
4. F. Solymosi, J. Sarkany, and A. Schauer, J. Catal., 46, 297 (1977).
5. H. Arai and H. Tominaga, J. Catal., 43, 131 (1976).
6. A. Ebitani, H. Niiyama, and E. Echigoya, J. Chem. Soc. Jpn., 1974, 1185.

(Received February 16,1979)