

Selective Catalytic Reduction of NO by CO over Supported Iridium and Rhodium Catalysts

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The catalytic reduction of NO with CO was investigated in the presence of oxygen over 16 supported metallic catalysts. Ir/WO₃, Ir/ZnO, and Rh/Al₂O₃ showed the pronounced activity even in excess amount of oxygen. The effect of preparation conditions on the activity of Ir catalysts was further studied and it was found that Ir/WO₃ prepared by loading of H₂IrCl₆ at 0.5 wt % Ir is the most active for the NO reduction with CO.

Three way catalysts are designed to reduce emissions of carbon monoxide, nitrogen oxides, and uncombusted hydrocarbons. Under lean conditions, certain hydrocarbons have been proved to act as selective reductants,¹⁻⁴ while CO and H₂ have not been regarded as selective reductant under lean conditions, since they are oxidized by O₂ rather than by NO under an oxygen-rich atmosphere. Recently, Burch et al. have found that the reduction of NO by H₂ could be carried out in an oxidizing conditions over Pt catalysts under an oxygen-rich atmosphere.^{5,6} Ogura et al. found that Ir/silicate could catalyze NO reduction by CO even in the presence of excess oxygen.⁷ Wang et al. reported that among Pt, Pd, Rh, and Ir noble metal catalysts, only Ir/ZSM-5 catalyst exhibited high activity for NO reduction by CO in the presence of excess oxygen.^{8,9} These are very interesting information since automotive exhausts always contain certain amount of CO. However, the catalysts for NO reduction with CO in the presence of excess oxygen have been received only a little attention and many questions still exist.

In the present study, the reduction of NO with CO by 7 metals, Ag, Cu, Fe, Ir, Pd, Pt, and Rh, supported on metal oxides has been investigated in the presence of excess O₂. The effect of 6 metal oxide supports on the catalytic activity of Ir and Rh were also investigated. The influence of the loading amount of metal and the starting Ir compound on the activity of the highly active Ir catalysts was further studied.

Rh or Ir supported on Ga₂O₃, In₂O₃, WO₃, ZnO, and ZSM-5, Ir supported on Ga₂O₃, and Ag, Cu, Fe, Pd, Pt, Rh, or Ir supported on Al₂O₃ were prepared by an impregnation method. Al₂O₃, Ga₂O₃, In₂O₃, WO₃, ZnO, or Na-ZSM-5 were impregnated with aqueous solution of acetate of Cu, chloride of Ag, Pd or Ir, nitrate of Fe or Rh, or ammonium nitrate of Pt in a rotary evaporator at 343 K. These catalysts were further calcined in air for 2 h at 773 K. Na-ZSM-5 (SiO₂/Al₂O₃ = 23.8) was supplied from Tosoh Co.Ltd. Metal loading amounts were 0.1, 0.3, 0.5, and 1.0 wt %. Unless otherwise stated, all the experiments were carried out using 0.5 wt % metal loading catalyst.

The reactant gases used were NO (1000 ppm), CO (1%) and O₂ (2%), and they were diluted by He. Prior to the runs, the catalysts were treated in the reactor at 773 K for 2 h and cooled to the reaction temperature in a stream of He. The reaction was carried out in a conventional flow reactor at W/F of 0.6 g s cm⁻³ and at 473, 523, and 573 K. The reactor was made of 9-mm diameter Pyrex glass tubing in which the catalyst sample of 0.5 g

was mounted on loosely packed quartz wool. The concentrations of N₂, N₂O, O₂, CO, and CO₂ in the outflow gas were determined using gas chromatographs (Shimadzu 6A and Ohkura 701) with porapak Q and molecular sieve 5A columns. The concentration of NO₂ was monitored using a UV-vis spectrophotometer (Hitachi Model 100-10).

Table 1 summarizes the conversion of NO to N₂ and/or N₂O in the catalytic reduction of NO (1000 ppm) by CO (1%) in the presence of O₂ (2%) over various metal catalysts supported on Al₂O₃ obtained at 473, 523, and 573 K. The pronounced activities for the reduction of NO are observed over Rh/Al₂O₃ even at lower temperature (473 K), while the selectivity for N₂O formation is higher than that for N₂ formation. The NO conversion for Rh/Al₂O₃ decreases with an increase in the reduction temperature. On the other hand, at higher temperature (573 K), Ir/Al₂O₃ and Cu/Al₂O₃ reveal high activities for N₂ formation in CO reduction of NO. On the basis of the results shown in Table 1, the effect of support on the catalytic activity of Ir and Rh catalysts is further investigated.

Table 1. The conversion of NO to N₂ or N₂O in the reduction of NO by CO over various metals supported on Al₂O₃

Catalyst	473 K		523 K		573 K	
	N ₂ /%	N ₂ O/%	N ₂ /%	N ₂ O/%	N ₂ /%	N ₂ O/%
Ag/Al ₂ O ₃	0	0	0	0	1.0	0
Cu/Al ₂ O ₃	3.4	16.8	7.8	41.5	11.5	47.7
Fe/Al ₂ O ₃	0	0	0.8	13.3	0.6	0
Ir/Al ₂ O ₃	0	0	5.1	0	14.6	0
Pd/Al ₂ O ₃	3.7	0	5.0	0	4.6	0
Pt/Al ₂ O ₃	0	0	4.4	11.1	1.6	0
Rh/Al ₂ O ₃	21.9	53.0	12.3	26.5	11.1	19.9

Reactants: NO (1000 ppm) – CO (1%) – O₂ (2%)

Table 2 summarizes the conversion of NO to N₂ and/or N₂O obtained over Ir and Rh supported on Al₂O₃, Ga₂O₃, In₂O₃, WO₃, ZnO, and ZSM-5. At 473 K, Rh/ZnO also shows the pronounced activities for NO reduction together with Rh/Al₂O₃. At 573 K, Ir catalysts supported on WO₃, ZnO, In₂O₃, and Ga₂O₃ reveal excellent activities for CO reduction of NO and these Ir catalysts show a higher selectivity for N₂ formation. Especially, Ir/WO₃ shows the highest value of N₂ selectivity at 523 K. On the basis of the results shown in Table 2, the effect of loading amount of Ir is further investigated over Ir/WO₃.

Table 3 summarizes the conversion of NO to N₂ and/or N₂O together with that of CO obtained at 523 K over Ir/WO₃ with 0.1, 0.3, 0.5, and 1.0 wt % Ir loaded. The conversion of NO to N₂ increases with an increase in the loading amounts of Ir and the N₂ formation increases drastically between 0.3 and 0.5 wt % Ir. The maximum value (82.1%) of N₂ formation is obtained at 0.5 wt % Ir. On the other hand, CO conversion is less than 24.5% at Ir loading below 0.3 wt %, while CO conversion exhibits 100% above 0.5 wt % Ir. From these results, it is found

Table 2. The conversion of NO to N₂ or N₂O in the reduction of NO by CO over various supported Ir and Rh catalysts

Catalyst	473 K		523 K		573 K	
	N ₂ /%	N ₂ O/%	N ₂ /%	N ₂ O/%	N ₂ /%	N ₂ O/%
Ir/Al ₂ O ₃	0	0	5.1	0	14.6	0
Ir/Ga ₂ O ₃	0	0	7.7	9.3	46.0	16.8
Ir/In ₂ O ₃	9.8	10.6	28.5	26.5	48.9	18.1
Ir/WO ₃	2.8	0	79.5	15.9	72.9	19.9
Ir/ZnO	0	0	40.9	16.4	66.3	23.0
Ir/ZSM-5	18.5	8.8	10.5	0	9.0	0
Rh/Al ₂ O ₃	21.9	53.0	12.3	26.5	11.1	19.9
Rh/In ₂ O ₃	1.3	0	10.1	10.2	5.5	0
Rh/WO ₃	8.9	0	13.0	23.0	–	–
Rh/ZnO	24.2	30.5	16.0	32.7	10.7	12.8
Rh/ZSM-5	15.1	0	29.9	31.4	14.3	27.8

Reactants: NO (1000 ppm) – CO (1%) – O₂ (2%)**Table 3.** Effect of Ir loading on conversions of NO to N₂ or N₂O and CO over Ir/WO₃

wt %	N ₂ /%	N ₂ O/%	CO/%
0.1	19.8	11.1	24.1
0.3	28.7	8.4	24.5
0.5	82.1	17.7	100
1.0	78.9	18.6	100

Reactants: NO (1000 ppm) – CO (1%) – O₂ (2%)

Reaction temperature: 523 K

that Ir/WO₃ with 0.5 wt % Ir loaded is the most available catalyst for NO reduction with CO, and then the loading amount of Ir is determined as 0.5 wt % and all experiments are carried out using 0.5 wt % metal loading catalyst.

Table 4 summarizes the effect of the starting Ir compound on the conversion of NO to N₂ and N₂O studied over Ir/WO₃ at 523 K. Ir/WO₃ prepared from H₂IrCl₆ shows the highest activity and stability on the reduction of NO with CO. Ir/WO₃ prepared from IrCl₄ also shows the high activity, while the catalyst is not so stable, since the NO conversion obtained at 2nd run is 30% lower than that at 1st run. It is found that H₂IrCl₆ is the most

Table 4. Effect of starting Ir compound on the conversion of NO to N₂ or N₂O in the reduction of NO by CO over Ir/WO₃

Starting Ir compound	1st run		2nd run	
	N ₂ /%	N ₂ O/%	N ₂ /%	N ₂ O/%
IrCl ₄	79.5	15.9	59.0	8.8
H ₂ IrCl ₆	82.1	17.7	78.6	16.4
IrCl ₃	60.0	6.2	58.9	13.3
[IrCl(NH ₃) ₅]Cl ₂	11.0	0	–	–

Reactants: NO (1000 ppm) – CO (1%) – O₂ (2%).

Reaction temperature: 523 K.

appropriate for the preparation of Ir/WO₃.

The catalytic reduction of NO with CO was investigated in the presence of excess oxygen over 7 metals supported on Al₂O₃. Ir and Rh supported on 6 metal oxides were also investigated. The pronounced activity on the NO reduction by CO was obtained over Ir/WO₃, Ir/ZnO, and Rh/Al₂O₃ even in excess amount of oxygen. The influence of the support, the loading amount of metal, and the starting Ir compound on the activity of the highly active Ir catalysts was further studied. These results suggest that Ir/WO₃ prepared by loading of H₂IrCl₆ at 0.5 wt % Ir is the most active for the NO reduction with CO.

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