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/WO_3, Ir/ZnO, and Rh/Al_2O_3 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/WO_3 prepared by loading of H_2IrCl_6 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 H_2 have not been regarded as selective reductant under lean conditions, since they are oxidized by O_2 rather than by NO under an oxygen-rich atmosphere. Recently, Burch et al. have found that the reduction of NO by H_2 could 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 O_2. 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 Ga_2O_3, In_2O_3, WO_3, ZnO, and ZSM-5, Ir supported on Ga_2O_3, and Ag, Cu, Fe, Pd, Pt, Rh, or Ir supported on Al_2O_3 were prepared by an impregnation method. Al_2O_3, Ga_2O_3, In_2O_3, WO_3, 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 ($SiO_2/Al_2O_3 = 23.8$) 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 O_2 (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 $0.6\,\mathrm{g\,s\,cm^{-3}}$ 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 N_2, N_2O, O_2, CO, and CO_2 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 NO_2 was monitored using a UV–vis spectrophotometer (Hitachi Model 100-10).

Table 1 summarizes the conversion of NO to N_2 and/or N_2O in the catalytic reduction of NO (1000 ppm) by CO (1%) in the presence of O_2 (2%) over various metal catalysts supported on Al_2O_3 obtained at 473, 523, and 573 K. The pronounced activities for the reduction of NO are observed over Rh/Al_2O_3 even at lower temperature (473 K), while the selectivity for N_2O formation is higher than that for N_2 formation. The NO conversion for Rh/Al_2O_3 decreases with an increase in the reduction temperature. On the other hand, at higher temperature (573 K), Ir/Al_2O_3 and Cu/Al_2O_3 reveal high activities for N_2 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 N_2 or N_2O in the reduction of NO by CO over various metals supported on Al_2O_3

Catalyst	473 K		523 K		573 K	
	N_2/%	N_2O/%	N_2/%	N_2O/%	N_2/%	N_2O/%
Ag/Al_2O_3	0	0	0	0	1.0	0
Cu/Al_2O_3	3.4	16.8	7.8	41.5	11.5	47.7
Fe/Al_2O_3	0	0	0.8	13.3	0.6	0
Ir/Al_2O_3	0	0	5.1	0	14.6	0
Pd/Al_2O_3	3.7	0	5.0	0	4.6	0
Pt/Al_2O_3	0	0	4.4	11.1	1.6	0
Rh/Al_2O_3	21.9	53.0	12.3	26.5	11.1	19.9

Reactants: NO (1000 ppm) – CO (1%) – O_2 (2%)

Table 2 summarizes the conversion of NO to N_2 and/or N_2O obtained over Ir and Rh supported on Al_2O_3, Ga_2O_3, In_2O_3, WO_3, ZnO, and ZSM-5. At 473 K, Rh/ZnO also shows the pronounced activities for NO reduction together with Rh/Al_2O_3. At 573 K, Ir catalysts supported on WO_3, ZnO, In_2O_3, and Ga_2O_3 reveal excellent activities for CO reduction of NO and these Ir catalysts show a higher selectivity for N_2 formation. Especially, Ir/WO_3 shows the highest value of N_2 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/WO_3.

Table 3 summarizes the conversion of NO to N_2 and/or N_2O together with that of CO obtained at 523 K over Ir/WO_3 with 0.1, 0.3, 0.5, and 1.0 wt % Ir loaded. The conversion of NO to N_2 increases with an increase in the loading amounts of Ir and the N_2 formation increases drastically between 0.3 and 0.5 wt % Ir. The maximum value (82.1%) of N_2 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 N_2 or N_2O in the reduction of NO by CO over various supported Ir and Rh catalysts

Catalyst	473 K		523 K		573 K	
	N_2/%	N_2O/%	N_2/%	N_2O/%	N_2/%	N_2O/%
Ir/Al_2O_3	0	0	5.1	0	14.6	0
Ir/Ga_2O_3	0	0	7.7	9.3	46.0	16.8
Ir/In_2O_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_2O_3	21.9	53.0	12.3	26.5	11.1	19.9
Rh/In_2O_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%) – O_2 (2%)

Table 3. Effect of Ir loading on conversions of NO to N_2 or N_2O and CO over Ir/WO_3

wt %	N_2/%	N_2O/%	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%) – O_2 (2%)
Reaction temperature: 523 K

that Ir/WO_3 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 N_2 and N_2O studied over Ir/WO_3 at 523 K. Ir/WO_3 prepared from H_2IrCl_6 shows the highest activity and stability on the reduction of NO with CO. Ir/WO_3 prepared from $IrCl_4$ 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 H_2IrCl_6 is the most appropriate for the preparation of Ir/WO_3.

Table 4. Effect of starting Ir compound on the conversion of NO to N_2 or N_2O in the reduction of NO by CO over Ir/WO_3

Starting Ir compound	1st run		2nd run	
	N_2/%	N_2O/%	N_2/%	N_2O/%
$IrCl_4$	79.5	15.9	59.0	8.8
H_2IrCl_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%) – O_2 (2%).
Reaction temperature: 523 K.

The catalytic reduction of NO with CO was investigated in the presence of excess oxygen over 7 metals supported on Al_2O_3. Ir and Rh supported on 6 metal oxides were also investigated. The pronounced activity on the NO reduction by CO was obtained over Ir/WO_3, Ir/ZnO, and Rh/Al_2O_3 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/WO_3 prepared by loading of H_2IrCl_6 at 0.5 wt % Ir is the most active for the NO reduction with CO.

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