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LIQUID PHASE CATALYTIC OXIDATION OF NITRIC OXIDE WITH NITRIC ACID

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Catalytic oxidation of nitric oxide with nitric acid was carried out in the presence of various metal salts. Copper, iron, cobalt and nickel ions had catalytic activity. The influences of temperature and contact time were examined. The possibility of the application to the pretreatment for the removal of nitrogen oxides was discussed.

It is an important problem to remove nitrogen oxides contained in industrial exhaust gases. Occupying more than 90 % out of the nitrogen oxides exhausted from many kinds of furnaces, nitric oxide has low reactivity and low solubility in water. It is desirable for reductive degradation in a liquid phase to oxidize nitric oxide to oxides with higher oxidation numbers such as N_2O_3 (equimolar mixture of NO and NO_2), NO_2 or N_2O_5 which are reactive and soluble in water. Nitrogen dioxide is dissolved in water according to (1)

$$2NO_2 \rightleftarrows N_2O_4, \quad N_2O_4 + H_2O \rightleftarrows HNO_2 + HNO_3 \qquad (1)$$

It is also known that the equimolar mixture of nitric oxide and nitrogen dioxide is dissolved in water to form nitrous acid[1]

$$NO + NO_2 \rightleftarrows N_2O_3, \quad N_2O_3 + H_2O \rightleftarrows 2HNO_2 \qquad (2)$$

Nitrous acid is easily reduced by certain reductants. So, it is industrially significant to oxidize nitrogen oxide in the exhaust gases to the equimolar mixture of NO and NO_2. As nitric oxide in low concentration is not easily autoxidized[2], catalysts such as charcoal, zeolite and silica gel have been used for the oxidation with oxygen. Other oxidizing agents such as permanganate, chlorite, hydrogen peroxide and ozone are also used for this purpose[3].

In this work, the authors tried the catalytic oxidation of nitric oxide with dilute nitric acid and studied the promotive effect of some transition metals. The effects of reaction temperature and contact time on the reaction were also investigated.

The composition of the reactant gas was 240 ppm of nitric oxide, 5 % of oxygen and nitrogen as balance. Nitric oxide was obtained from Seitetsu Chem. Co. The flow rate of the mixed gas was 1.2 l/min. The reactant aqueous solutions contained 1 mol/l of various metal salts and 1 mol/l of nitric acid. Used salts were $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Mn(NO_3)_2$, $Cr(NO_3)_3$, $Al(NO_3)_3$ and KNO_3.

The reaction was carried out by a flow method with a glass bubbling tower of which dimension was 3.5 cm in inner diameter and 120 cm long with a glass filter at the bottom. Contact time defined as (the volume of the reactant gas retained in the reactant solution) / (the flow rate of the reactant gas) was controlled in the range 1.5 – 30 sec by the variation of the volume of the reactant solution. The reaction temperature was 15 – 100°C. The concentrations of NO and NO_2 were determined by a $NO-NO_x$ analyzer (Toshiba-Beckman Ltd., Model 951A) by which NO and NO_x ($NO + NO_2$) were measured based on chemical luminescence.

The results of the reactions at 90°C with 400 ml of reactant solutions are shown in Table 1 together with the NO_2/NO ratios at the outlet. Just after the beginning of gas flow, the concentrations of NO and NO_2 at the outlet varied with time owing to the dissolution of them. The variations of the outlet concentrations of NO and NO_2 with the reaction time are shown in Fig. 1. The values in Table 1 were measured at more than 30 min after the beginning of the reactions, reaching constant values. In the system with 1 mol/l of $Cu(NO_3)_2$ and 1 mol/l of HNO_3, NO was oxidized to NO_2 up to the ratio of 9.87. As the ratio was 3.20 in the case with 3 mol/l of HNO_3 without metal ion, apparently copper ion had catalytic activity. A reactant solution of $Cu(NO_3)_2$ without HNO_3 showed a low NO_2/NO ratio, so the nitrate ion in copper nitrate scarecely contributed to the oxidation reaction. The removal of oxygen from the reactant gas did not lower the reactivity for the oxidation. Moreover, the solution of $CuSO_4$ as well as distilled water did not convert NO to NO_2. These facts

Table 1. Outlet concentrations of NO and NO_2 and NO_2/NO ratios after the oxidation with metal salts + nitric acid at 90°C. The inlet NO was 240 ppm and the contact time was 30 sec.

Solution		Outlet (ppm)		NO_2/NO
Metal salt	Nitric acid	NO	NO_2	
$Cu(NO_3)_2$	1 mol/l	45	445	9.87
$Cu(NO_3)_2$	–	200	70	0.35
$CuSO_4$	–	235	20	0.09
$CuSO_4$	1	125	210	1.68
Water	–	235	30	0.13
–	1	200	57	0.29
–	3	100	320	3.20
$Fe(NO_3)_3$	1	65	425	6.54
$Co(NO_3)_2$	1	70	380	5.43
$Ni(NO_3)_2$	1	60	390	6.50
$Mn(NO_3)_2$	1	85	285	3.35
$Cr(NO_3)_3$	1	110	235	2.14
$Al(NO_3)_3$	1	90	335	3.72
KNO_3	1	110	280	2.55

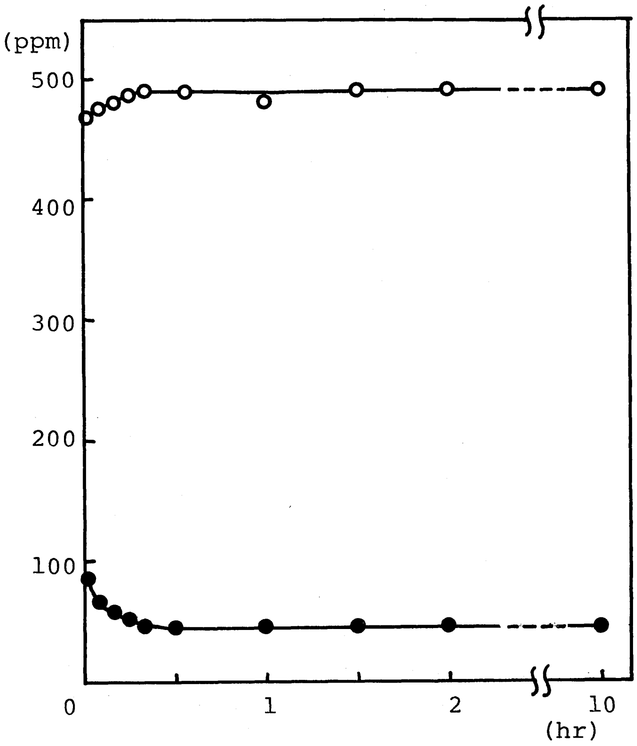

Fig. 1. Variations of the outlet concentrations of NO and NO_2 with the reaction time through the oxidation of NO with 1 mol/l of $Cu(NO_3)_2$ and 1 mol/l of HNO_3 at 90 °C. Concentration of NO, ● ; NO_2, o . The inlet NO was 240 ppm and the contact time was 30 sec.

suggest that the oxidation with oxygen rarely proceeded. It is presumed that NO is oxidized as the following, being catalyzed by metal ions.

$$NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O \qquad (3)$$

This oxidation reaction was maintained for more than 10 hours constantly.

In the $Cu(NO_3)_2 + HNO_3$ system, the ratio of the increase of NO_2 (ΔNO_2) to the decrease of NO (ΔNO), $\Delta NO_2/\Delta NO$ was equal to 2.28. As the value of $\Delta NO_2/\Delta NO$ predicted from equation (3) is 3.00, the obtained value is too small. It seems to be the reason that the produced NO_2 was dissolved in the reactant solution with NO and formed nitrous acid as equation (2).

Next the activities of the metal ions were compared. From the values of NO_2/NO shown in Table 1, the activities of them were evaluated as the order of Cu > Fe, Co, Ni > Mn, Al > Cr, K. Among the investigated metal ions, the copper ion was the most effective. The solution of KNO_3 and HNO_3 oxidized NO only to the ratio as well as dilute HNO_3 alone, so the potassium ion is considered to have no activity.

When SO_2 was present in the reactant gas, the oxidation of the SO_2 to SO_3 with nitric acid preceded the oxidation of NO. The presence of 5 % of carbon dioxide did not disturb the oxidation of NO.

The temperature dependences of the outlet NO_2/NO and the percentage of the conversion defined as (the decreased amount of NO) / (the inlet amount of NO) x 100 in the

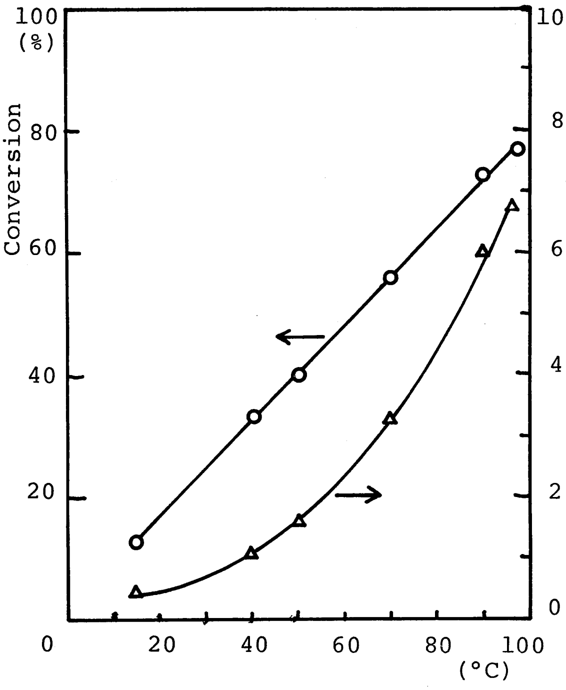

Fig. 2. Effect of the temperature on the oxidation of NO with 1 mol/l of $Cu(NO_3)_2$ + 1 mol/l of HNO_3. Percentages of the conversion, o ; NO_2/NO ratios, ▲ . The inlet NO was 240 ppm and the contact time was 30 sec.

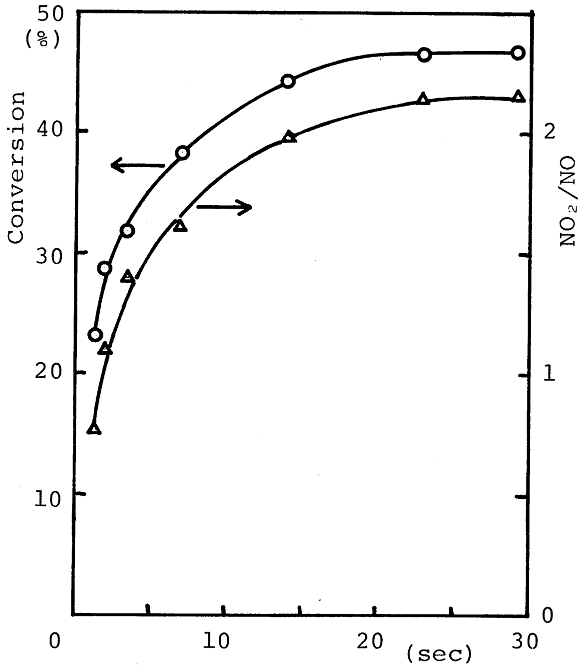

Fig. 3. Effect of the contact time on the oxidation of NO with 1 mol/l of $Cu(NO_3)_2$ + 1 mol/l of HNO_3 at 60°C. Percentages of the conversion, o ; NO_2/NO ratios, ▲ . The inlet NO was 240 ppm.

system with $Cu(NO_3)_2$ and HNO_3 are shown in Fig. 2. As the conversion percentage increased linearly with temperature, the NO_2/NO increased markedly in higher temperature range. In this case, Fig. 2 shows that the reaction had such activity as the ratio exceeded one at about 50°C.

In Fig. 3 the effect of the contact time is shown in the system with $Cu(NO_3)_2$ and HNO_3 at 60°C. The NO_2/NO ratio or the conversion percentage increased significantly with contact time in the range from 1.5 to 5 sec, but gradually near 15 sec and became constant in the range over than 20 sec. This behavior suggests that the reaction had reached equilibrium. The reaction

$$NO(gas) + 2HNO_3(aq.) \rightleftarrows 3NO_2(gas) + H_2O(liq.)$$

is endothermic by 13 kcal/mol, therefore it is expected that the rise of the temperature displaces the equilibrium to the right hand. In fact, the value of NO_2/NO was 2.12 at 60°C and 9.87 at 90°C in the presence of copper nitrate at the contact time of 30 sec.

In this system, the mixed gas of equimolar NO and NO_2 was obtained under mild conditions such as the temperature of 60°C and the contact time of 2 sec. This method has a disadvantage that the concentrations of NO_x at the outlet become larger than those at the inlet. It is an advantage in this method, however, that the oxidation of NO with nitric acid progresses at low temperature and in short contact time in comparison with the catalytic oxidations with charcoal and silca gel.

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