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ABSORPTION OF NITROGEN OXIDES WITH AMMONIUM SALTS

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Absorptions of an equimolar mixture of NO and NO_2 in an aqueous solution of ammonium salts and with a cation-exchange resin substituted by ammonium ion were investigated by a flow method. Ammonium salts such as phosphate, benzoate, and oxalate were found effective for the removal of nitrogen oxides. Effects of temperature and time of contact were examined.

Catalytic reduction in a gaseous phase and oxidative absorption in a liquid phase are representative of the methods for the removal of nitrogen oxides from industrial exhaust gases.[1] However, these methods are troublesome because of the poisoning of catalysts for the former and the treatment of the waste solutions for the latter. Nitric oxide which occupies more than 90 % of nitrogen oxides exhausted from furnaces has low reactivity and low solubility in water. But, when the nitric oxide in exhaust gases is partially oxidized to an equimolar mixture of NO and NO_2, it is easily dissolved in water to form nitrous acid.[2]

$$NO + NO_2 + H_2O \rightleftarrows 2HNO_2 \qquad (1)$$

It is also known that nitrogen dioxide dissolves in water and forms nitrous acid and nitric acid according to (2)

$$2NO_2 + H_2O \rightleftarrows HNO_2 + HNO_3 \qquad (2)$$

In the previous paper, the authors described that nitric oxide was catalytically oxidized with nitric acid in a liquid phase.[3]

In the present paper, we report on the removal of nitrogen oxides by means of the absorptions of an equimolar mixture of NO and NO_2 in an aqueous solution of ammonium salts and with a cation-exchanger substituted by ammonium ion.

The composition of the reactant gas was 120 ppm of NO, 120 ppm of NO_2 and nitrogen as balance. Gases NO and NO_2 were obtained from Seitetsu Chem. Co. The flow rate of the mixed gas was 0.88 – 1.20 l/min. The ammonium salts used were CH_3COONH_4, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$, $C_6H_5COONH_4$, $(COONH_4)_2$, $(NH_4)_2SO_4$, and $(NH_4)_2CO_3$. The concentrations of the ammonium salts in the aqueous solutions were 1 N with respect to ammonium ion. However, because of the low solubility, 0.6 N oxalate solution was used exceptionally. Moreover, a cation-exchange resin IRC-50

(Rohm and Haas Co., carboxylic type) substituted by ammonium ion was examined as the remover of nitrogen oxides. The reaction was achieved 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. The time of contact 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 0.5 – 8 sec by varying the volume of the solutions. The reaction was carried out at 15 – 100°C. The concentrations of NO and NO_2 were determined with an NO-NO_X analyzer (Toshiba-Beckman, Model 951A) based on chemiluminescence. The concentrations of NO_2^- and NO_3^- in the reactant solutions which had taken up nitrogen oxides were determined by sulfanilic acid method[4] and brucine method[5] respectively with a spectrophotometer (JASCO, UVIDEC-1).

The percentages of NO, NO_2 and NO_X(NO + NO_2) trapped with individual ammonium salts at 20°C are shown in Table 1 in which the flow rate of the reactant gas is 1.2 l/min, and the volume of the reactant solution is 400 ml. The time of contact is 7 sec. The solution of CH_3COONH_4 (1 mol/l) removed 85.8 % of NO_X. The percentage of removal of NO_X is somewhat lower for $(NH_4)H_2PO_4$ but is more than 90 % for $(NH_4)_2HPO_4$ and $(NH_4)_3PO_4$. It is also high for $C_6H_5COONH_4$. In spite of the low concentration, 0.3 mol/l solution of $(COONH_4)_2$ removed 86.5 % of NOx. High percentage of removal was also obtained for $(NH_4)_2CO_3$ in contrast to $(NH_4)_2SO_4$, a salt of a strong acid. The results of the removal with NaOH and distilled water are also shown as the reference. The cation-exchange resin substituted by ammonium ion which was packed in a glass column of 3.5 cm diameter and 16 cm long removed 80 % of NO_X. In this case the space velocity was 450 hr^{-1}.

Table 1. Percentages of absorption with ammonium salts at 20°C.

Ammonium salt	Percentage of removal		
	NO	NO_2	NO_X
CH_3COONH_4	75.8	95.8	85.8
$NH_4H_2PO_4$	37.5	83.3	60.4
$(NH_4)_2HPO_4$	92.5	97.5	95.0
$(NH_4)_3PO_4$	86.6	100.0	93.3
$C_6H_5COONH_4$	86.7	99.2	92.9
$(COONH_4)_2$	72.9	100.0	86.5
$(NH_4)_2SO_4$	41.7	88.3	65.0
$(NH_4)_2CO_3$	88.3	95.0	91.7
Amberlite IRC-50-NH_4	77.5	85.8	81.3
NaOH	92.5	97.1	94.8
Water	8.3	37.5	22.9

When the reactant gas was passed with the flow rate of 0.88 l/min through the 1 mol/l solution of CH_3COONH_4 for 3 hr, the total amount of NO_X was 1.55×10^{-3} mol in the reactant gas. As the percentage of the removal obtained from the NO-NO_X analyzer was 85.8 %, the amount of NO_X absorbed with the solution of the ammonium salt was 1.33×10^{-3} mol. On the other hand, the amounts of NO_2^- and NO_3^- in the solution obtained from the colorimetric analyses were 1.13×10^{-3} mol and 0.28×10^{-3} mol, respectively. As the sum of these values was in a good agreement with the absorbed amount of the NO_X, most of the absorbed NO_X was present in the forms of NO_2^- and NO_3^- in the solution. The proportion of NO_2^- was 80 % and that of NO_3^- was 20 %, which indicated simultaneous occurrence of the reactions (1) and (2).

The salts $(NH_4)_3PO_4$ and $(NH_4)_2CO_3$ decompose at a temperature lower than 100°C and releases gaseous ammonia. When neutralized with nitrous acid, CH_3COONH_4 releases acetic acid which is volatile at the reaction temperature. The salt of a

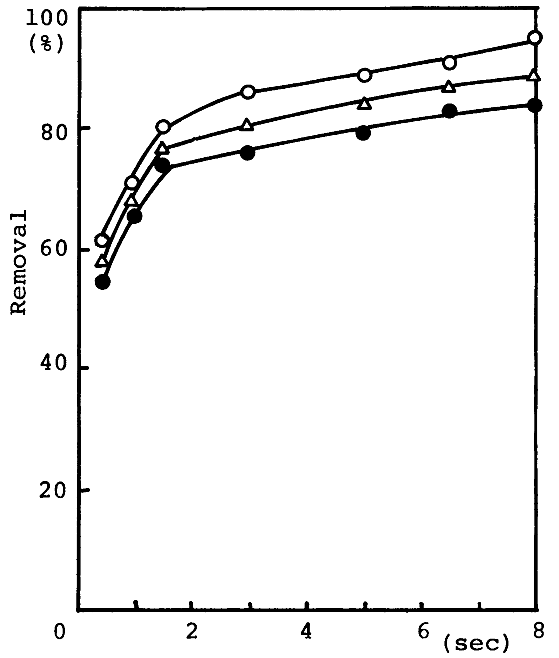

Fig. 1. Effect of the time of contact on the absorption of nitrogen oxides with 0.5 mol/l $(NH_4)_2HPO_4$ at 20°C. Percentages of the absorption of NO, ● ; NO_2, o ; and NO_x, △ . The inlet concentrations of NO and NO_2 were 120 ppm respectively.

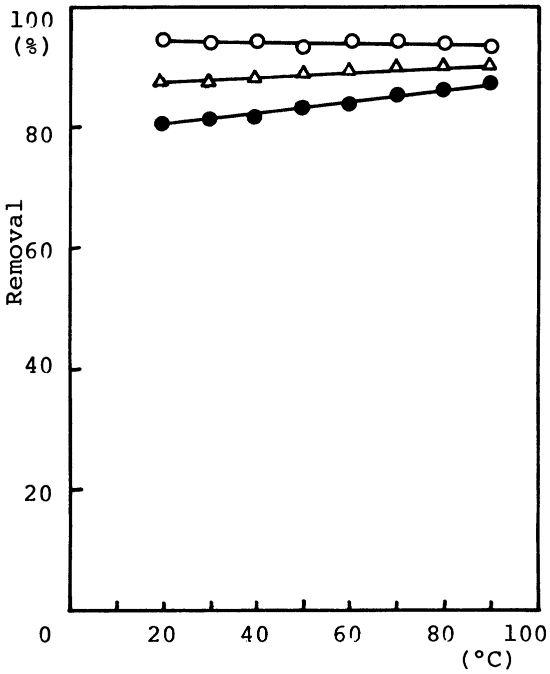

Fig. 2. Effect of the temperature on the absorption of nitrogen oxides with 0.5 mol/l $(NH_4)_2HPO_4$. Percentages of the absorption of NO, ● ; NO_2, o ; and NO_x, △ . The time of contact was 8 sec. The inlet concentrations of NO and NO_2 were 120 ppm respectively.

strong acid had low reactivity for the removal. $(NH_4)_2HPO_4$, $C_6H_5COONH_4$, $(COONH_4)_2$, and the cation-exchange resin substituted by ammonium ion will be useful in practice, because they have no disadvantages described above. In particular, $(NH_4)_2HPO_4$ is so useful to remove both NO and NO_2 in high extent and in the same proportion.

The dependence of the removal on the time of contact with 0.5 mol/l solution of $(NH_4)_2HPO_4$ at 20°C is shown in Fig. 1. In the range shorter than 2 sec, the percentages of the removal were improved significantly with the time of contact, but in longer range varied gradually. The changes of the percentages of the removal for NO and NO_2 were approximately parallel. Fig. 2 shows the temperature dependence of the removal in the range 20 – 90°C. The percentage of removal for NO_2 was invariable and that for NO improved slightly with temperature.

When the mixture of NO and NO_2 passed through the aqueous solution of ammonium salts, HNO_2 and HNO_3 were formed according to equations (1) and (2). Next these acids would react with ammonium salts as the following equations

$$HNO_2 + NH_4OA \rightleftarrows NH_4NO_2 + HOA \qquad (3)$$

$$HNO_3 + NH_4OA \rightleftarrows NH_4NO_3 + HOA \qquad (4)$$

where HOA was an acid.

Reactions (1) – (4) progressed so fast that more than 80 % of dilute NO_x was absorbed in 2 sec of contact. Addition of ammonia reproduces the ammonium salt from the acid formed by reactions (3) and (4).

$$HOA + NH_3 \rightleftarrows NH_4OA \qquad (5)$$

Most of the formed NH_4NO_2 is expected to decompose thermolytically to nitrogen and water as shown in equation (6)[6]

$$NH_4NO_2 \rightleftarrows N_2 + 2H_2O \qquad (6)$$

The work on this reaction is in progress.

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