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REMOVAL OF NITROGEN OXIDES FROM AIR BY CHEMICALS-IMPREGNATED CARBONS

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Abstract – Fixation of nitrogen oxides (NO_x) in air onto granular activated carbon impregnated with chemicals was attempted to improve removal efficiency of NO_x by activated carbon adsorption. Nitric oxide (NO) and nitrogen dioxide (NO_2), were tried to remove by a flow test. Fixed-bed adsorption breakthrough curves were obtained when some kinds of carbon were used. The amount adsorbed of NO_2 changed with the amount and kinds of metallic salts impregnated. Chemicals-impregnated carbons were prepared from a commercial activated carbon. Among obtained carbons, the one which showed the highest selectivity for NO_x was chosen, and its performance with the change in humidity was determined. Removal mechanism of NO_2 was estimated, and the carbon impregnated with potassium hydroxide was found to be superior to any other carbon tested. The amount of the adsorbed NO and that produced by the reduction of NO_2 were determined from the breakthrough curves.

Key words: *Adsorption, Chemicals-Impregnated Carbon, Evolution Ratio of NO_x, NO_x Removal, Reduction Ratio*

INTRODUCTION

Nitrogen oxides, so-called NO_x, discharged as combustion waste gases are one of the origins of air pollution and acid rain. In spite of many environmental regulations, NO_x in air has been increasing gradually, especially in urban areas. Therefore, it is necessary to develop suitable treatment methods of NO_x before discharging them to our environment.

Regarding the removal of NO_x, many papers were reported, for example, by use of various adsorbents, such as activated carbon fiber (ACF) [Mochida et al., 1985c] and zeolite [Naruse et al., 1979], and by selective catalytic reduction (SCR) in the presence of NH_3 [Mochida et al., 1987; Mochida et al., 1985a; Mochida et al., 1985b]. As an efficient removal method, activated carbon adsorption method was also tried to use [Gray and Do, 1992; Urano et al., 1977], and some results for surface-modified carbon and other adsorbents were reported [Hashida and Nishimura, 1975; Inui et al., 1982; Kaneko et al., 1985; Kapteijn et al., 1984; Mochida et al., 1991; Mochida et al., 1985d; Okuhara and Tanaka, 1986; Yamashita et al., 1991].

Activated carbon is a carbonaceous material having fine porous structure. Its surface is non-polar and its adsorption ability is essentially based on van der Waals force, i.e., the adsorption is physical. Therefore, activated carbon shows generally poor performance for the adsorption of components with a low boiling point, e.g., carbon monoxide and ammonia. However, the chemical adsorption and/or chemical reactions with impregnated chemicals were tried to bring about a great increase in the adsorption capacity of the carbon by impregnation of chemicals such as acid, alkali and metallic salts onto the internal surface and into the pores of the carbon [Yanai, 1983]. Though physical adsorption onto bare surface of the carbon was decreased by the impregnation, ill-smelling or harmful compounds in the air decomposed or neutralized. The authors have been investigated the deodorization of H_2S, CH_3SH and $(CH_3)_3N$ by chemicals-impregnated carbons before [Takeuchi et al., 1988].

In this paper, results on the removal of NO_x especially NO_2, by an activated carbon, are presented focusing on the improvement of the removal efficiency.

EXPERIMENTAL

1. Preparation of Surface-Modified Activated Carbon

As shown in Fig. 1, modified carbon samples were prepared from a commercial granular activated carbon (AG-80), produced by Ebara Corp., Japan. The original carbon was a coconut-shell base one, having mean particle size of 8.60 mm, 1,250 m^2/g in BET surface area, 0.321 cm^3/g in pore volume and 1.28 g/cm^3 in particle density, respectively. The granular carbon was crushed to a sieve fraction of 16/22 mesh and was treated in nitrogen stream for 1 hour at 383 K and then 4 hours at 413 K. Hereafter, this sample is abbreviated as G_o. Next, 10 grams of G_o were subjected to impregnation of metallic salts by soaking into 300 ml of aqueous solutions of LiOH, NaOH, KOH and RbOH, respectively, held in a flask, under the evacuation for three hours. After removing the solutions by filtration, the carbon particles on a filter were washed quickly with deionized water and stored in a dryer at 383 K for a day. Then they were dried again in nitrogen stream. For these samples, the chemical symbols and molarity of solutions soaked are suffixed, to express the kind of salts impregnated and the normality of solutions in which the samples were soaked. For example, $G_{K\text{-}1.0}$ means that the sample was immersed in an aqueous solution of KOH of 1.0 N.

The amount impregnated and the pore volume of each sam-

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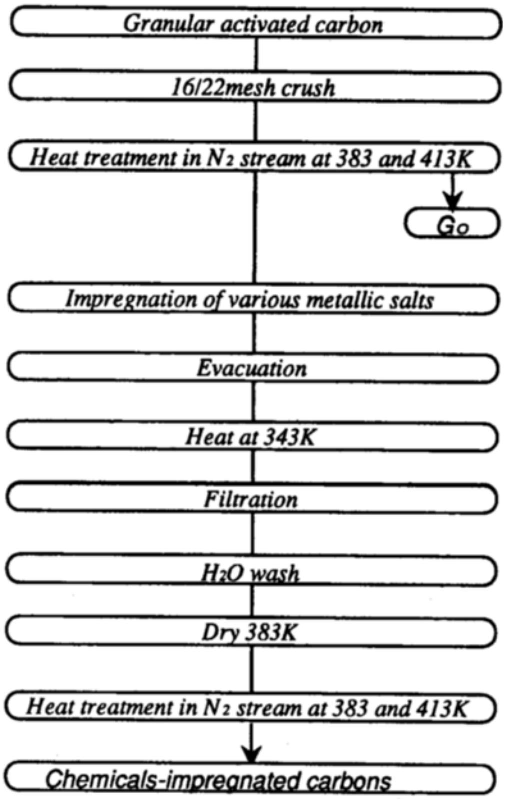

Fig. 1. Flow of impregnation processes.

ple are listed in Table 1. The amount impregnated in these samples were measured in the following manner, i.e., 0.5 g of each sample was immersed in the 250 ml of 0.1 N aqueous solution of HCl and degassed under vacuum for a day, then the chemicals extracted were determined by use of a polarized Zeeman atomic absorption spectrometer (Z-6000, Hitachi, Co., Ltd., Japan).

2. Experimental Method

A schematic diagram of the experimental apparatus is shown in Fig. 2. Each sample prepared by the procedure described above was packed in a glass column of 1.28×10^{-2}m i.d., to a height of 1.00×10^{-2} m. Temperature was kept at 298 K using a constant temperature bath. Diluting NO_x gas with the air fed by a blower, the air stream of a constant NO_x concentration and a constant flow rate was supplied to the column. Unless otherwise described, its relative humidity was kept always at 80 % by a vaporizer. The concentration of NO_x in the effluent air from the carbon bed was measured by a NO_x-O_2 analyzer for combustion waste gases (NOA-7000, SHIMADZU CORP., Japan). Experiments were carried out under the following conditions, i.e., linear flow rate of 0.596 m/s, the concentration of nitric oxide (here after NO) gas of 20 ppm when it was the target gas and the concentration of NO_2 of 100 ppm when it was the target gas, at the entrance of the adsorption column.

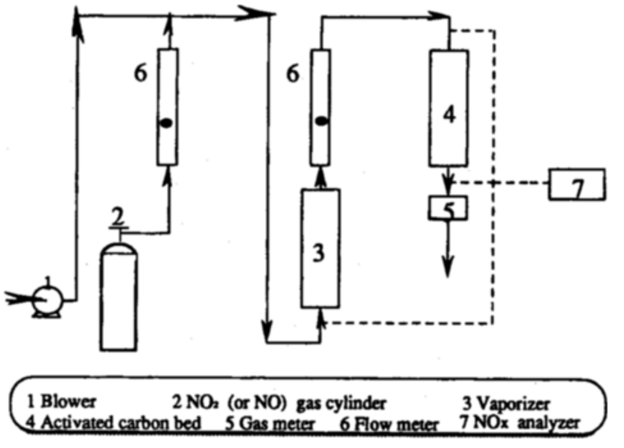

Fig. 2. Schematic diagram of experimental apparatus.

The adsorbed amount of NO_2, q, and the evolution-ratio of NO, E, was calculated from the results using the following equations;

$$q=\frac{M}{R\cdot T}\int_0^t[v\cdot C_0\cdot\{(1-C^*/C_0)-E\}/W]dt$$

$$E=(C^*_{NO}-C_{0NO})/(C_{0NO})$$

Taking into account of the desorption of NO from the adsorbent by reduction of NO_2 adsorbed, the amount of NO evolved was deducted from the amount of the adsorbed NO_2.

RESULTS AND DISCUSSION

1. Comparison of the Removal of NO_x between Various Impregnated Carbons

Since NO gas is in a supercritical state at ambient temperature and pressure, it doesn't condense at the micropore of activated carbon [Kaneko et al., 1985]. Therefore, it is expected that its amount adsorbed is small and that the type of adsorp-

Table 1. Amount impregnated and pore volume of samples used

Name of samples	Amount impregnated		Pore volume	Name of samples	Amount impregnated		Pore volume
	[kg/kg]	[mol/kg]	[cc/g]		[kg/kg]	[mol/kg]	[cc/g]
G_o	–	–	0.2515	$G_{Li-0.1}$	4.61×10^{-4}	1.92×10^{-2}	0.2378
$G_{Rb\ 4.9}$	3.72×10^{-2}	3.63×10^{-2}	0.2241	$G_{Li\ 1.0}$	9.37×10^{-4}	3.91×10^{-2}	0.2395
$G_{K\ 0.1}$	1.89×10^{-3}	3.37×10^{-2}	0.2439	$G_{Li-4.5}$	1.37×10^{-3}	5.76×10^{-2}	0.2271
$G_{K\ 1.0}$	3.52×10^{-3}	6.28×10^{-2}	0.2505	$G_{Na-0.1}$	3.84×10^{-2}	9.60×10^{-1}	0.2612
$G_{K\ 2.0}$	4.39×10^{-3}	7.82×10^{-2}	0.2505	$G_{Na-1.0}$	5.59×10^{-2}	1.40	0.2642
$G_{K\ 4.5}$	6.08×10^{-3}	1.08×10^{-1}	0.2668	$G_{Na\ 2.0}$	3.03×10^{-1}	7.58	0.2561
$G_{K\ 10}$	7.30×10^{-3}	1.30×10^{-1}	0.2375	$G_{Na-4.5}$	1.12	2.80×10^{1}	0.2310
$G_{K\ 18}$	10.3×10^{-3}	1.85×10^{-1}	0.2361				

**Pore volume for each sample was determined by mercury porosimetry.

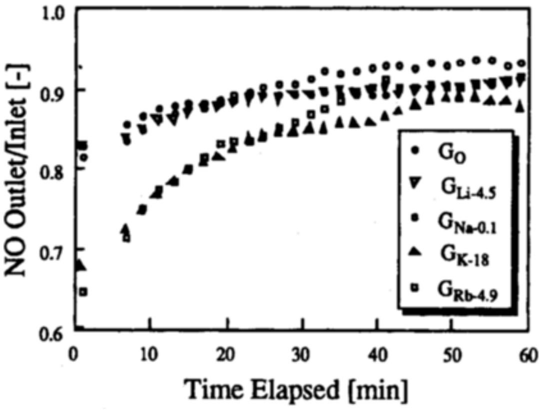

Fig. 3. Breakthrough curves for original and impregnated carbons.

tion onto the activated carbon will be mostly by chemisorption, and the impregnated carbon is expected to adsorb larger amount of NO than common activated carbon. Fig. 3 shows concentration changes of NO with time, i.e., breakthrough curves, when original (G_o) and four kinds of impregnated carbons were used under the humid conditions. From the figure, it is clear that $G_{K\ 18}$ and $G_{Rb-4.9}$ show better adsorption performance for NO than that of G_o at an earlier time.

The results of NO_2 removal by various impregnated carbons under humid condition are shown in Figs. 4-6. Regarding the amount of chemicals impregnated and the amount of NO_2 removed by the carbons, there seems to exist optimal values in all cases. It was found that when the more chemicals were impregnated, more NO_2 was adsorbed on the adsorbents at first. However, the latter part of these graphs always shows decreasing tendency, i.e., more chemicals impregnated made the decrease in the amount adsorbed greatly. The transfer of NO_2 into particles seems to be hindered by the blockage of macropore when larger amount of chemicals is impregnated, consequently, the adsorbed amount decreases. The pore volume of each sample is shown in Table 1 and the blockage of macropore can be also known from this table. As can be seen from Table 2, the carbon impregnated with potassium hydroxide showed the best performance among all the carbon samples used for NO_2 removal.

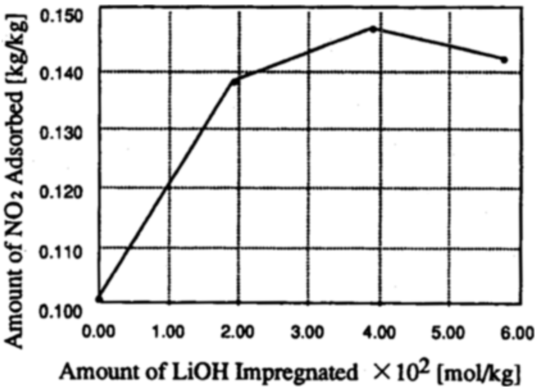

Fig. 4. Relation between amount of LiOH impregnated and amount of NO_2 adsorbed.

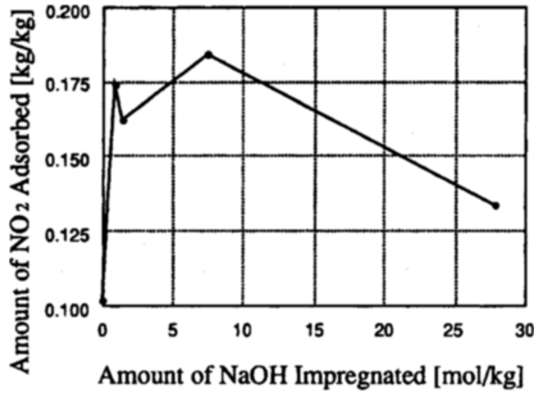

Fig. 5. Relation between amount of NaOH impregnated and amount of NO_2 adsorbed.

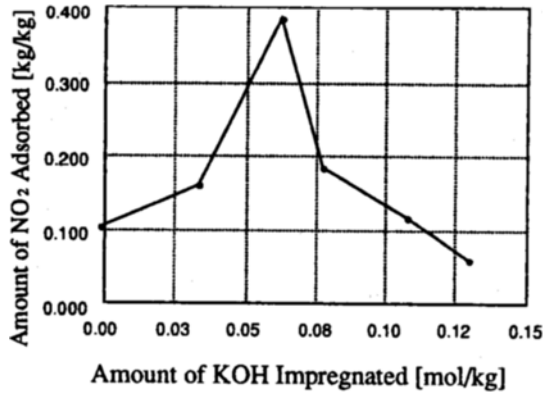

Fig. 6. Relation between amount of KOH impregnated and amount of NO_2 adsorbed.

2. Comparison of G_o with $G_{K\ 4.5}$ under Dry and Humid Conditions

Table 3 shows the results of NO_2 removal by G_o and $G_{K-4.5}$ under dry (10% R.H.) and humid (80% R.H.) conditions. It the case of $G_{K-4.5}$, the amount adsorbed of NO_2 under the dry

Table 2. Amount of NO_2 adsorbed by original and each modified carbon

Name of samples	Reduction ratio [%]	Amount of NO_2 adsorbed [kg/kg]
G_o	17.49	0.1012
$G_{Li\ 0.1}$	16.18	0.0923
$G_{Li-1.0}$	16.47	0.1467
$G_{Li\ 4.5}$	9.43	0.1420
$G_{Na-0.1}$	27.52	0.0757
$G_{Na-1.0}$	16.19	0.1617
$G_{Na-2.0}$	19.74	0.1838
$G_{Na-4.5}$	13.73	0.1329
$G_{K\cdot 0.1}$	15.48	0.1184
$G_{K\ 1.0}$	24.48	0.3847
$G_{K\cdot 2.0}$	19.70	0.1841
$G_{K\ 4.5}$	13.10	0.1157
$G_{K\cdot 1.0}$	10.53	0.0591
$G_{Rb\ 4.9}$	23.64	0.1321

Amount of NO_2 was calculated until C/C_0 of NO_x=0.8.

Table 3. Comparison of results for nitrogen dioxide removal under dry and humid condition

Name of samples	Reduction ratio [%]	Amount adsorbed of NO_2 [kg/kg]
G_o	17.49	0.1012
$G_{K\ 4.5}$	13.10	0.1157
G_o^d	46.53	0.0885
$G_{K-4.5}^d$	8.92	0.1191

※ "d" denotes under dry condition.

condition was about the same as that obtained under the humid condition. On the other hand, the results differed each other for G_o. Also, the difference in the reduction ratio under the dry and the humid conditions for G_o was much larger than that for $G_{K\ 4.5}$. Namely, the reduction ratio of G_o under the dry condition was considerably larger than that obtained under the humid condition. Here, the reduction ratio means the ratio of total NO reduced to total NO_2 fed to the bed.

Fig. 7 shows changes in the discharge ratio of NO with time when G_o was used under the dry and the humid conditions. The ratio is defined as the ratio of the total amount of NO at the outlet of the adsorption column to NO_2 fed to the inlet, measured at each time. The discharge ratio for G_o under the dry condition was larger than that obtained under the humid condition. Since NO_2 adsorbed on the activated carbon surface will be desorbed in the form of NO, these results suggest that the amount of NO_2 adsorbed by the activated carbon decreases when the original carbon is used under the dry condition. Fig. 8 illustrates the changes in the discharge ratio of NO with time when $G_{K-4.5}$ was used under the dry and humid conditions. The values under the dry condition were a little larger than that obtained under the humid condition.

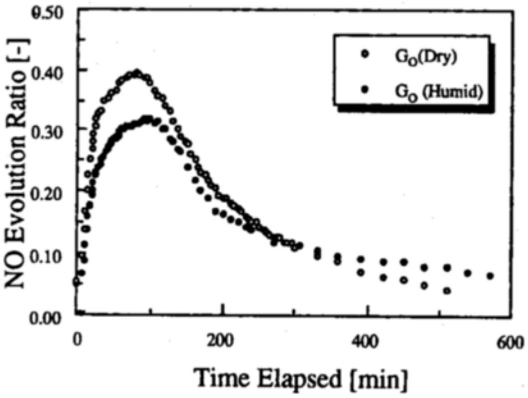

Fig. 7. Changes of evolution ratio of NO with time by G_o.

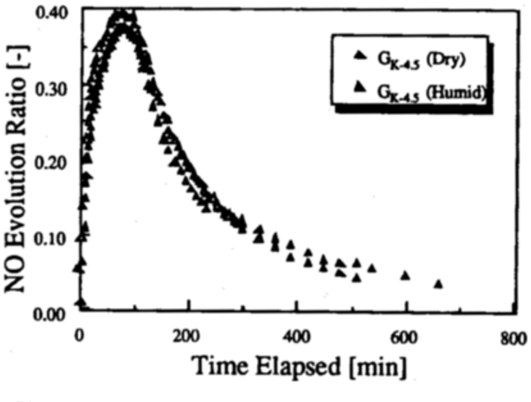

Fig. 8. Changes of evolution ratio of NO with time by $G_{K\ 4.5}$.

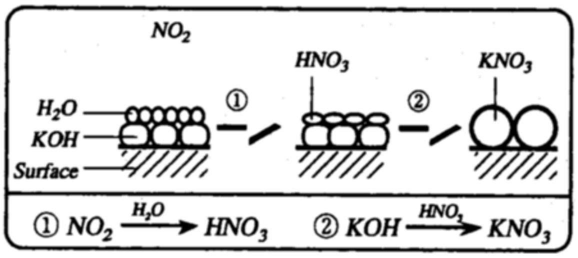

Fig. 9. Schematic diagram of removal mechanism of NO_2 by the carbon impregnated with potassium hydroxide.

From these results, the removal mechanism of NO_2 can be estimated as follows, i.e., NO_2 reacts with water adsorbed on the surfaces of pores of activated carbon particles to form nitric acid and then the nitric acid reacts with potassium hydroxide or potassium carbonate. Though the reaction requires the existence of water, results for $G_{K-4.5}$ didn't show a great difference between two cases in contrast to the case of G_o, because the potassium hydroxide absorbs moisture from the air. The removal mechanism of NO_2 is illustrated schematically in Fig. 9. Thus, the removal of NO_2 by the carbon impregnated with potassium hydroxide may not be influenced by ambient humidity.

CONCLUSION

The impregnation of alkali metal salts on activated carbon was found to the effective for NO_x removal by adsorption. Among the impregnated salts, potassium hydroxide showed the best performance for the removal. Also, the performance was not affected by the change in humidity. However, the excess amount of impregnation decreased NO_2 removal probably due to the blockage of macropore and the coverage of internal surface of activated carbon. Since the potassium hydroxide is available at cheap price, the activated carbon impregnated with potassium hydroxide seems to be suitable for NO_x removal if a proper amount of the salts is impregnated.

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NOMENCLATURE

C_0 : concentration of influent NO_2 [ppm]
C^* : concentration of effluent NO_2 [ppm]
C_{0NO} : concentration of influent NO [ppm]
C^*_{NO} : concentration of effluent NO [ppm]
E : evolution ratio of NO [–]

M	: molecular weight of NO_2 [−]
q	: amount of NO_2 adsorbed [g]
R	: gas constant [$l\cdot$atm/mol$\cdot$K]
T	: temperature [K]
t	: time elapsed [min]
W	: weight of activated carbon [g]
v	: volumetric gas flow rate [l/min]

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