Reduction of NO at Very Low Concentration in Air with NH_3 at Room Temperature over a Series of Calcined Pitch Based Active Carbon Fibers

Isao Mochida,* Shizuo Kawano, Motohiro Hironaka, Shunsuke Yatsunami,
Yozo Korai, Yuji Matsumura,† and Masaaki Yoshikawa†
Institute of Advanced Material Study, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816
†*Research & Development Center, Osaka Gas Co., Ltd, 6-19-9, Torishima, Konohana-ku, Osaka 554*

(Received January 12, 1995)

Catalytic activities of a series of pitch based active carbon fibers (ACFs) were examined for the reduction of NO (10 ppm) with NH_3 (20 ppm) at 293 K. A particular ACF of 840 $m^2\ g^{-1}$ surface area exhibited the excellent activities after the calcination at 1123 K, providing conversions of 75 and 47 % in dry and wet (80 % relative humidity) air, respectively, at W/F of 5×10^{-3} g min ml^{-1}. The ACF of the largest surface did not show the largest activity.

Acid rain is still a major environmental problem in the developed as well as developing countries.[1] NO exhausted from automobiles is now the major origin for the acid rain and air pollution in the urban environment in the developed countries.[2] NO liberated in the atmosphere should be reduced by any methods. The low concentration of NO, ambient temperature, high humidity and large volume of air to be treated exclude the developed technologies as any effective approaches.[3,4] The active carbon has been known to catalyze the reduction of NO with ammonia around 393 K.[5] The present authors have reported the high catalytic activity of activated carbon fibers (ACF) for the reduction of NO (400 ppm) in the flue gas with ammonia at room temperature as well as around 373 K.[6,7] A pitch based ACF showed higher activity in wet air than any other ACFs probably because of its hydrophobic properties.[8,9]

In the present study, catalytic activities of a series of further calcined pitch based activated carbon fibers were examined at 293 K in the reduction of NO of low concentration (10 ppm) in air with ammonia (20 ppm). The main objective of the present study is to find the best pitch based ACF for the reduction of NO with NH_3 into N_2 at room temperature. Roles of humidity are most concerned for the practical application of the ACF in the present objective. Hence, influences of the calcination were examined at 873 ~ 1273 K to enhance the hydrophobic nature of the ACF surface.

A series of pitch based active carbon fibers (OG series) were supplied by Osaka Gas Co. As-received active carbon fibers and the heat treated ones were used in this study. The heat treatment was carried out at 873 (OG-5~20A-H873, H; heat treatment and the same manner of abbreviation to other temperatures), 973, 1023, 1073, 1123, 1173 and 1273 K for 1h by a heating rate of 10 K min^{-1} in the nitrogen atmosphere. Table 1 shows some properties of as-received ACFs. Their surface area and pore volume were determined through N_2 adsorption.

Table 1. Some properties of pitch based carbon fibers

ACFs as-received	Surface area $m^2\ g^{-1}$	Pore volume ml g^{-1}	Mean pore diameter Å
OG-5A	480	0.25	13.6
OG-7A	690	0.35	10.5
OG-8A	840	0.41	10.4
OG-10A	1060	0.52	10.4
OG-20A	1550	0.81	10.6

The reaction of NO with NH_3 was carried out under the flow of dry or wet air as a carrier gas using a U shaped fixed bed flow type glass reactor (10 mm diameter) where 0.5 g of active carbon fiber was closely packed in 80 mm length. The ratio of NO to NH_3, total flow rate (F) and the contact time (W/F) were 0.5 (NO =10 ppm), 100 ml min^{-1} , and 5×10^{-3} g min ml^{-1}, respectively. Humidity in air was controlled by mixing the air at 100 % relative humidity (rh) and dry air. The relative humidity was measured by a humidity meter (CHINO NH-U type). NO concentration was analyzed continuously at the inlet and the outlet of the reactor, using a NO_x meter (ECL-77, Yanagimoto Co., Kyoto). Details were described in previous papers.[10,11] Stationary NO conversion was determined when NO concentration at the outlet of the reactor showed the steady state. NO_2 was never found in the product. N_2 and N_2O concentration was not measured.

Figure 1 illustrates the reaction of NO with NH_3 in dry and wet (80 % rh) air over OG-series ACF calcined at 1073 and 1123 K. NO in dry air was completely removed (100 % conversion) for 3.5 h after the reaction started over OG-5A- H1073 and then NO started to leak, its conversion decreasing gradually for successive 5 h to be 67 % at the stationary state. Excess NH_3 was found to leak in the product gas. Approximately NO reacted with the equimolar NH_3. The stationary conversion was stable for further 10 h at shortest. Since as-received OG-5A exhibited a stationary conversion of 51 %, the positive influence of calcination on activity is clearly shown.

OG-ACF of larger surface area, OG-7A and OG-8A, exhibited significantly higher activities than OG-5A after calcination at 1073 K. However further larger surface areas of OG-10A and OG-20A lowered considerably the activity after the same calcination. So far OG-8A of which as-received surface area was 840 $m^2\ g^{-1}$ provided the largest activity. It should be noted that larger surface areas did not always exhibit the largest activity. Some surface chemistry and pore structure appear to be more influential. A little higher temperature of calcination at 1123 K, further increased the activity of OG-7A and 8A in the dry air, providing conversions of 73 and 75 %, respectively. Some decrease of surface area was observed by the calcination.

The humidity of 80 % reduced the activity of all ACFs markedly as shown also in Figure 1. Nevertheless OG-7A and 8A calcined at 1123 K exhibited 38 and 47 % conversions, respectively.

Figure 2 summarizes the influences of the calcination temperature on the activities of OG-5A, 7A, 8A ACFs in wet as well as in dry air. Significant and marked influences of the calcination on the activity in dry and wet air, respectively, are definitely noted. The temperature of 1123 K appeared optimal for the calcination of OG-7A and 8A to give the largest activities in air, while 1073 K appeared best for OG-5A of smaller surface

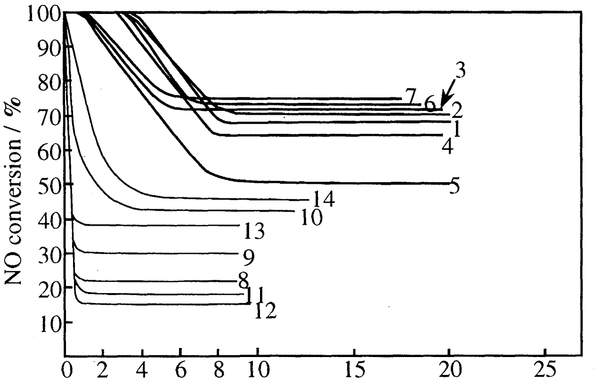

Figure 1. Conversion of NO in dry and wet air at room temperature over Calcined pitch based ACFs

NO : NH_3 = 1 : 2 (NO = 10 ppm), O_2 = 10%, N_2 balance

Temp. = 293 K, W/F = 5×10^{-3} g min ml^{-1}

Dry air (rh = 0 %)		Wet air (rh = 80 %)	
1. OG-5A-H1073	5. OG-20A-H1073	8. OG-5A-H1073	12. OG-20A-H1073
2. OG-7A-H1073	6. OG-7A-H1123	9. OG-7A-H1073	13. OG-7A-H1123
3. OG-8A-H1073	7. OG-8A-H1123	10. OG-8A-H1073	14. OG-8A-H1123
4. OG-10A-H1073		11. OG-10A-H1073	

area.

A particular pitch ACF of OG-8A showed the highest conversions of 75 and 47 % in the dry and wet (80 % rh) air, respectively. Such activities may appear high enough for the practical application to the reduction of NO in atmosphere over the pitch ACF.

The surface area of OG-5A, -7A, -8A calcined at 873 - 1273 K were also shown in Figure 2. The calcination increased the area at 873 K. Higher temperatur gradually decreased the area. Pore volume of ACFs decreased monotonously by the calcination. The active site on the ACF for NO reduction with NH_3 is not clear yet. However a small number of very active site can be introduced on the ACF surface by removing the major parts of oxygen functional groups which are introduced at the activation of pitch fiber to increase the surface area. Such a control of oxygen functional groups on the ACF may restrict the hydrophilic nature of its surface which brings about the strong poisoning by H_2O adsorption from humid air.

There appears an adequate extent of activation for the largest activity of pitch ACF after the calcination. Basically larger surface may lead to the larger activity. However the activation at high temperature tends to introduce pores of smaller mouth and less oxygen functional groups. Very small pores are useless for the catalytic reaction because of diffusion control and H_2O filling. Less oxygen functional groups induced on the ACF surface may mean the introduction of the less number of active sites after their removal. The last assumption suggests that the active site may be surface carbon of free valence. The calcination at too high temperature is generally believed to reduce the surface area and remove the active site by graphitic shrinkage although such graphitization is not detected by X-ray diffraction. Surface characterization of calcined ACF is now under investigation.

The present authors reported that such calcination increased the catalytic activities of ACFs for the oxidation of NO as well as SO_2 in air.[12,13] Common active sites are suggested. Mechanistic study is now in progress.

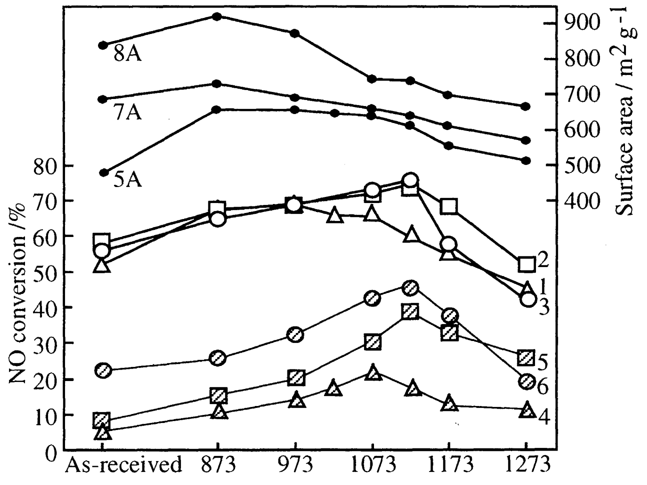

Figure 2. Conversion of NO in dry and wet air at room temperature over calcined pitch based ACFs and surface area of the ACFs. NOconversion was measured at about 15 ~ 30 h after the reaction started.

NO : NH_3 = 1 : 2 (NO = 10 ppm), O_2 = 10 %, N_2balance

Temp. = 293 K, W/F = 5×10^{-3} g min ml^{-1}

Dry air (rh = 0 %),		Wet air (rh = 80 %)	
1. OG-5A (△)	3. OG-8A (○)	4. OG-5A (▲)	5. OG-7A (▨)
2. OG-7A (□)		6. OG-8A (⊘)	

References and Notes

1 M. Grove and W. Sturn, *Ceram. Eng. Sci. Proc.*, **10**, 325 (1989).

2 W. Held, A. Konig, T. Riehter, and L. Puppe, *SAE Paper*, **1990**, 900496.

3 T. Sera, *Jpn. Petrol. Inst. Symposium*, **1991**, 32.

4 H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, and M. Tabata, *Appl. Catal.*, **64**, L1 (1990).

5 H. Juntgen and H. Kuhl, *Chemistry and Physics of Carbon*, Marcel Dekker INC., New York, (1989), Vol. 22, p 161.

6 I. Mochida, S. Kawano, H. Fujitsu, and T. Maeda, *Nippon Kagaku Kaishi*, **3**, 275 (1992).

7 I. Mochida, H. Fujitsu, S. Hisatsune, S.Kisamori, I. Shiraishi, and S. Ida, *Jpn. Petrol. Inst. Jour.*, **36**, 394 (1993).

8 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity, 2nd ed.*, Academic Press INC., London, (1982), p 263.

9 S. Kawano, S. Kisamori, I. Mochida, H. Fujitsu, and T. Maeda, *Nippon Kagaku Kaishi*, **6**, 694 (1993).

10 I. Mochida, S. Kawano, and T. Maeda, *Nippon Kagaku Kaishi*, **9**, 1177 (1991).

11 S. Kawano, S. Kisamori, I. Mochida, H. Fujitsu, S. Fujiyama, M. Komatsu, and T. Aoyama, *Jpn. Inst. Energy*, **72**, 1101 (1993).

12 I. Mochida, S. Kisamori, M. Hironaka, S. Kawano, Y. Matsumura, and M. Yoshikawa, *Energy & Fuels*, **8**, 1341 (1994).

13 S. Kisamori, K. Kuroda, S. Kawano, I. Mochida, Y. Matsumura, and M. Yoshikawa, *Energy & Fuels*, **8**, 1337 (1994).