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Characterization of Nitrogen-containing Active Carbon Catalysts for SO_2 Removal

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Physical and chemical properties of nitrogen-containing active carbons (ACs), having a much higher activity and capacity for SO_2 adsorption than commercial ACs, were investigated to define suitable properties for SO_2 removal. The capacity of nitrogen-containing ACs for SO_2 adsorption correlates with the amount of their surface basic groups. However, the amount of basic surface groups for the ACs is practically the same as that for commercial ACs, indicating that the ACs have another characteristic property effective for SO_2 removal. A study on the chemical state of surface nitrogen atoms by means of an X-ray photoelectron spectrometer has revealed that surface nitrogen species are effective for SO_2 adsorption.

Recently active carbons (ACs) have been used for simultaneous removal of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from flue gas discharged from stationary combustion equipments.[1-3] In this process SO_x is adsorbed on AC and removed as ammonium sulfate through reaction with NH_3 added in the flue gas,[3] NO_x being reduced to N_2 and H_2O by NH_3. However, those ACs developed so far are available only at low space velocities below 1000 h^{-1}, because of their low catalytic activity for SO_2 adsorption at temperatures effective for NO_x removal. Some of the present authors[3] found a new type of AC effective for SO_2 removal and developed a novel catalyst for the simultaneous removal of SO_x and NO_x by allowing AC to support metal salts effective for NO reduction with NH_3. The ACs developed were prepared from nitrogen-containing compounds such as polyacrylonitrile so as to contain some amounts of nitrogen atoms. It was also found, however, that the capacity of ACs for SO_2 removal is dependent highly on their activating conditions.

A number of mechanisms have been proposed for the catalytic oxidation of SO_2 on AC.[4-8] Daytyan[4] has indicated that the oxygen reversibly adsorbed on AC will oxidize SO_2 to SO_3. Siedlewski[5] has shown that free radicals on AC act as active centers in the chemisorption of SO_2. Kitagawa *et al.*[6] have found that the capacity for SO_2 removal does not depend on the surface area of AC but on the amount of oxygen atoms in AC. The work by Yamamoto *et al.*[7,8] has also shown that the capacity is dependent on preparation conditions and raw materials for AC rather than on the surface area of AC. Then, it was estimated by Kamino *et al.*[9,10] that basic surface group functions are activation points of oxidative chemisorption for SO_2 adsorption. Sano and Ogawa[11] have shown that for AC catalysts with higher activity for SO_2 removal, certain impurities on AC, such as surface nitrogen species, seem to have a good effect on catalytic activity.

The ACs studied in this work are designed to contain a few percent nitrogen atoms. Accordingly, nitrogen species in AC seem to play an important role in the process of SO_2 removal. Activating processes have been known to have an effect on physical and chemical properties of AC.[12,13] It is considered that various properties, especially the chemical state of nitrogen species in AC, are also affected by activating processes. In this work, physical and chemical properties of ACs prepared from polyacrylonitrile were investigated to characterize appropriate surface properties of AC for SO_2 removal.

Experimental

Catalysts. Polyacrylonitrile (100 g) was placed in a reactor made of quartz (length: 500 mm; diam.: 60 mm). The reactor was capable of rotating at desired speeds. Carbonization treatments were performed at 250 °C in an N_2 flow (1 l/h). Activation treatments were performed in the temperature range 400—1000 °C in the presence of water vapor. In the activating process, water (80 ml/h) was vaporized with a conventional vaporizer and supplied into the reactor with

Table 1. Activating conditions and nitrogen content of the AC catalyst used for SO_2 removal

Run	Activating temp/°C	Activating time/min	Nitrogen content/%	
			Bulk	Surface
1	400	60	—[a]	—[a]
2	500	30	14.6	7.8
3	600	30	10.3	5.1
4	700	30	8.4	3.7
5	750	30	8.0	3.0
6	800	15	11.0	3.4
7	800	30	7.4	2.4
8	800	40	5.5	—
9	800	50	4.5	—
10	800	60	3.7	1.4
11	850	30	—	—
12	900	15	—	—
13	900	30	5.1	1.5
14	900	60	—	—
15	950	30	—	—
16	1000	10	4.7	1.2
17	1000	15	4.1	0.9
18	1000	30	2.9	0[b]

a) No analysis was performed. b) No nitrogen atoms were detected by XPS.

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nitrogen (600 ml/h). The duration of activation was in the range 10—60 min. Some ACs now in commercial use for SO_2 removal were also used as reference. The AC catalysts studied are summarized in Table 1.

Activity and Capacity Measurement. The following reaction conditions for activity and capacity measurement was previously established as suitable for development of new processes which make higher space velocities available for SO_2 removal. An AC sample (diam.: about 1.2 mm) of 20 ml was placed in a flow reactor made of stainless steel (length: 300 mm; diam.: 20 mm). Activity and capacity measurements were then carried out at 200 °C at a space velocity of 5000 h^{-1}.[3] The gas mixture used consisted of 500 ppm SO_2, 500 ppm NH_3, 5 vol% O_2, 10 vol% H_2O, and N_2 balance. The analysis for SO_2 was made by means of an NDIR type SO_x analyzer.

Measurement of Catalytic Properties. Measurements of surface area and pore size distribution were carried out by the BET method (CARLO ERBA Sorptomatic 1800) and with a porosimeter (AMINCO 60000 PSI). Benzoic and hydrochloric acids were used to measure the amount of basic groups in AC, sodium hydroxide being used to measure that of acidic groups. For measuring the amount of benzoic acid adsorbed, 0.5 g of sample was dried under vacuum at 110 °C and then immersed in 50 ml of ethyl alcohol solution of benzoic acid (10 mol m^{-3}) for 48 h at room temperature. The amount of benzoic acid adsorbed was determined by titration with sodium hydroxide standard solution (10 mol m^{-3}).[9,14] Similar methods were used to measure amounts of hydrochloric acid and sodium hydroxide adsorbed. Surface chemical properties of AC such as chemical composition and chemical state were obtained by using an X-ray photoelectron spectrometer (Dupont 650 B) and Al anode. Measured areas of spectra, or measured heights in some cases, were used for determing surface elemental compositions, as demonstrated in several recent papers.[15-17] A CHN Corder (Yanaco MT-2) was also used to determine the chemical composition of AC.

Results and Discussion

Activity and Capacity of AC. Figure 1 shows the activity and capacity of ACs for SO_2 removal. The ACs prepared from polyacrylonitrile are superior in activity and capacity to the commercial ACs. However, their capacity is dependent highly on activating conditions. In this work the capacity of AC is defined as the shortest reaction time that brings about 100% SO_2 removal in the activity measurement. For the commercial ACs the capacity is defined as the shortest reaction time for 40% SO_2 removal, because of their lower catalytic activity for SO_2 removal.

Physical Properties. Figure 2 shows the relationship between the capacity and activating temperature of AC. The activating time used was 30 min. The highest capacity is obtained when the AC is activated at 800 °C. A change in capacity of AC with surface area of AC is shown in Fig. 3. The capacity does not correlate with the surface areas, though the surface area is dependent on activating conditions. Figure 4 shows pore size distributions for the ACs and commercial ACs. Similar pore size distributions are shown between these ACs. No correlation is found between the capacity and pore size distribution. These results seem to indicate that the SO_2 removal capacities of the ACs as well as usual AC catalysts depend on surface chemical propeties rather than on surface physical properties. Thus chemical properties of the ACs were then studied.

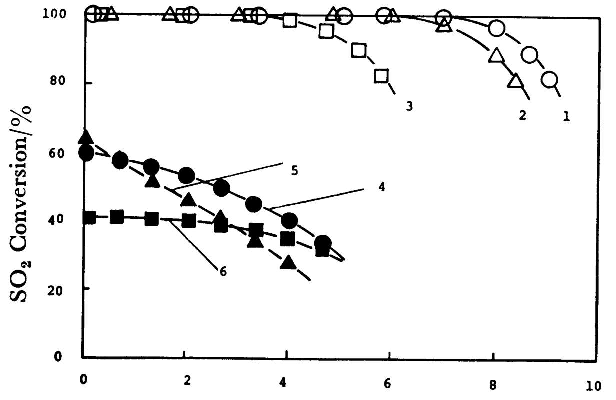

Fig. 1. Activity and capacity of AC used for SO_2 removal.

○, △, □: AC prepared from polyacrylonitrile, ●, ▲, ■: commercial AC.

Activating conditions: 1) 800 °C, 30 min, 2) 900 °C, 30 min, 3) 700 °C, 30 min,

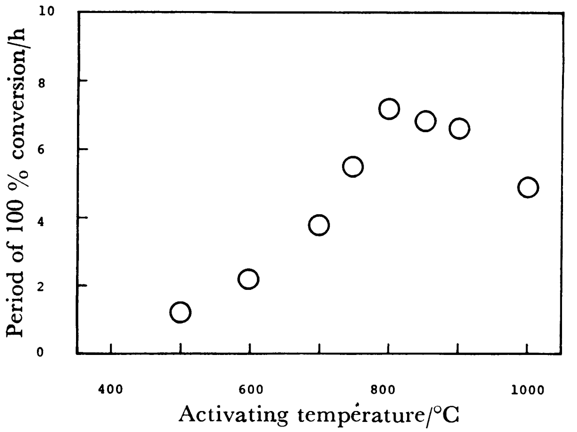

Fig. 2. Effect of activating temperature on capacity of the AC.

Activating conditions: activating time: 30 min, H_2O (vapor): 100 l/h, N_2: 600 ml/h

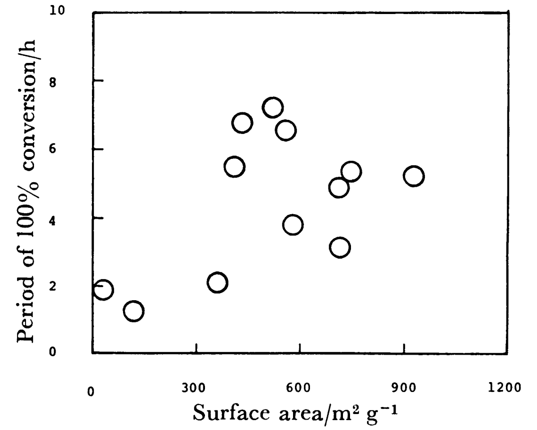

Fig. 3. Effect of surface area on capacity of the AC.

Basic and Acidic Surface Group. Figure 5 shows the

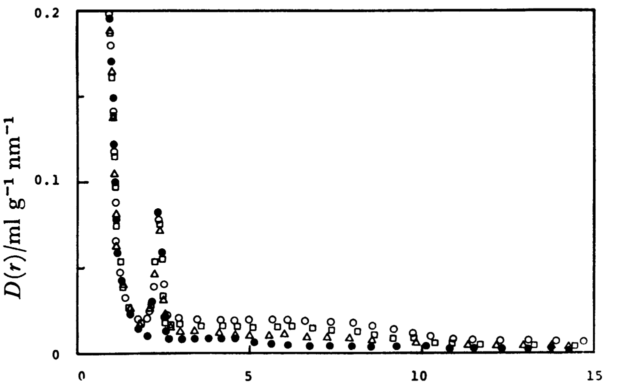

Fig. 4. Pore size distribution of AC used for SO_2 removal. $D(r)$: Pore size distribution function, ○, △, □: AC prepared from polyacrylonitrile. ●: Commercial AC.

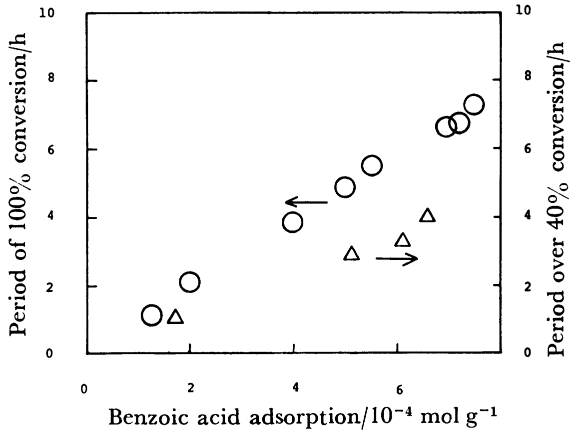

Fig. 5. Effect of benzoic acid adsorption on capacity of the AC.
○: AC prepared from polyacrylonitrile, △: commercial AC.
Capacities of the AC and commercial AC were defined as periods of 100% and over 40% conversion for SO_2 removal, respectively.

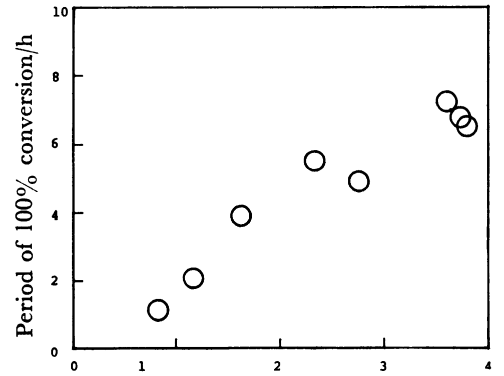

Fig. 6. Effect of hydrochloric acid adsorption on capacity of the AC.

correlation between the capacity and the amount of basic surface groups of the ACs as measured by using benzoic acid. The capacity increases with increase in benzoic acid adsorption, indicating that basic surface groups of AC are effective for the SO_2 adsorption. A similar trend was observed in a case using hydrochloric acid (Fig. 6), though with lowered correlation as compared with that shown in Fig. 5. On the other hand, the amount of acidic surface groups of the ACs decreases with increase in the capacity as shown in Fig. 7, indicating that acidic surface groups are not effective for the capacity. Amounts of benzoic acid adsorbed for the commercial ACs are 1.7—6.5 × 10^{-4} mol/g-AC and almost the same as those obtained for the ACs which have much higher activities and capacities for SO_2 removal (Fig. 5). These results seem to indicate that the ACs have another characteristic property effective for SO_2 removal, though the presence of basic surface groups is one of important necessities for the high performance catalyst for SO_2 removal. Amounts of sodium hydroxide adsorbed for the commercial ACs are 1—4 × 10^{-5} mol/g-AC, less than those for the ACs prepared (Fig. 7).

Nitrogen and Oxygen Species. As already mentioned, the ACs studied are designed to contain some amounts of nitrogen species, and hence it is considered that the nitrogen species in the ACs furnishes another property effective for SO_2 removal. A recent work by Kobayashi[18] has indicated that nitrogen species in ACs prepared from polyacrylonitrile exist in the states of C–N and N–N chemical bonds. A previous study[3] using an X-ray photoelectron spectrometer (XPS) has shown existence of two possible surface chemical states C–N and N–N, with the third state, more effective for SO_2 removal, left undefined.

Figure 8 shows change in nitrogen content in the ACs with activating temperature. The nitrogen content decreases with increase in activating temperature. When the same activating temperature is used, the nitrogen content decreases with increasing activating time as shown in Fig. 9. On the other hand, the capacity of the ACs increases up to the maximum with increasing

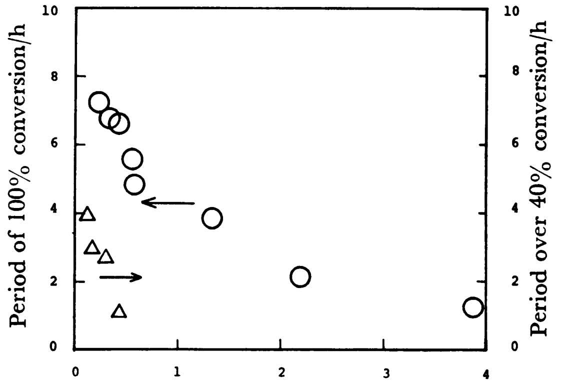

Fig. 7. Effect of hydroxide adsorption on capacity of the AC.
○: AC prepared from polyacrylonitrile, △: commercial AC.
Capacities of the AC and commercial AC were defined as periods of 100% and over 40% conversion for SO_2 removal, respectively.

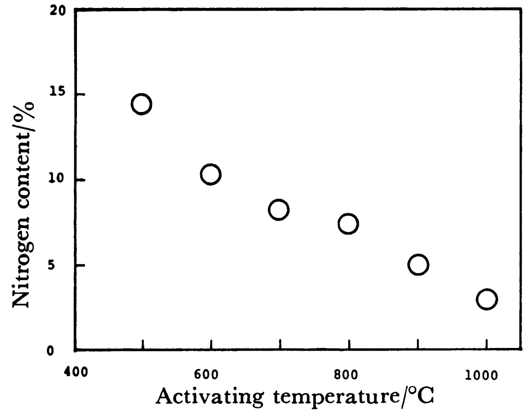

Fig. 8. Effect of activating temperature on nitrogen content in the AC.
Activating conditions: activating time: 30 min, H_2O (vapor): 100 l/h, N_2: 600 ml/h.

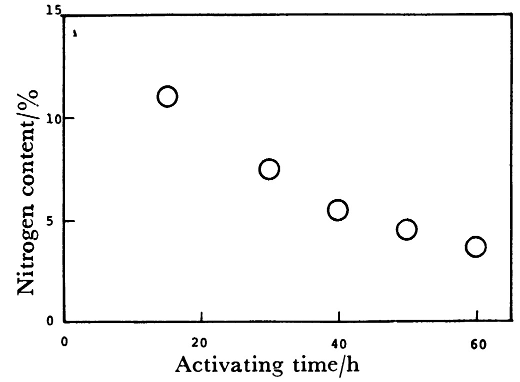

Fig. 9. Effect of activating time on nitrogen content in the AC.
Activating conditions: activating temperature: 800 °C. H_2O (vapor): 100 l/h, N_2: 600 ml/h.

reaction time and then decreases gradually.

Two peaks on N 1s photoelectron spectra were observed for the surface of the ACs, their binding energies being 396.1 and 397.5 eV. The higher binding energy peak (397.5 eV) seems to correspond to the chemical state of C–N bond, from a comparison with XPS spectra of polyacrylonitrile and other compounds which involve the chemical state of C–N bond,[19] whereas the lower binding energy peak seems to correspond to the chemical state of N–N bond.[20] The AC activated at 800 °C for 30 min has the highest capacity for SO_2 removal and gives a lower binding energy peak of maximum intensity (peak area). With the ACs having lower capacity for SO_2 removal, the intensity of lower binding energy peak is lower than that of the ACs with higher capacity. These results seem to indicate that the chemical state of N–N bond is more effective for SO_2 adsorption than that of C–N bond.

Table 1 also shows a comparison of amounts of nitrogen atoms present on the surface and in the bulk as measured by using XPS and CHN Corder, respectively. These results indicate that nitrogen species still exist on outer surface layers of AC particles though the amount of nitrogen atoms on surface layers is much less than that in the bulk. The amount of nitrogen atoms on surface layers decreases with increase in activating temperature. XPS shows that there is no detectable amount of nitrogen atoms on outer surface layers of the AC particles activated at 1000 °C for 30 min.

Oxygen species on surface are also known to affect the activity and capacity of AC for SO_2 removal.[6] No correlation is, however, found between the oxygen content on surface layers as measured by XPS and the capacity for SO_2 removal. Amounts of oxygen atoms on surface layers increase with increasing surface area. No chemical state of oxygen in surface functional groups is clear because of smaller chemical shifts in O 1s photoelectron spectra. Broader peaks of O 1s spectra on the ACs seem to support existence of more than two kinds of oxygen functional groups (acidic and basic) on the surface of the ACs.

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