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Adsorption of Hydrogen Sulfide on N-Containing Activated Carbon

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N-Containing activated carbon (N-CAC) was prepared by impregnating activated carbon with N-containing additives. Adsorption isotherms of hydrogen sulfide on N-CACs were obtained by a gravimetric method at 30°. A positive correlation between N content and specific adsorption of hydrogen sulfide at an equilibrium pressure of 50 Torr was found. It is considered that the adsorption of hydrogen sulfide resulted in the volume filling of micropores of N-CAC, based on application of the Dubinin-Astakhov equation to the adsorption isotherms. The finding that the net differential heat of adsorption and differential molar entropy of adsorption decreased with increasing degree of filling of micropores indicated that the micropores of N-CAC were successively filled with hydrogen sulfide from the smallest pores to the largest ones, and that hydrogen sulfide molecules were compactly filled in the micropores at an early stage of filling.

Keywords——hydrogen sulfide; N-containing activated carbon; volume filling; net differential heat of adsorption; differential molar entropy of adsorption; Dubinin-Astakhov equation; degree of freedom

Preparation and application of N–CAC were investigated for the first time by Sano *et al.*[1] We describe here the preparation of N–CAC and its application to the removal of hydrogen sulfide, which has an offensive odor. The thermodynamics of adsorption of hydrogen sulfide on N–CAC are also discussed in this paper.

Experimental

Preparation of N-CAC——The additives for N-introduction were ammonium acetate (1, 2, 3 M solution), ammonium carbonate (1, 2, 3 M solution), urea (1, 2, 3 M solution), *n*-butylamine (1, 2, 3 M solution), methylol-melamine-urea (6, 12, 25%(w/v) solution), methylol-urea (25%(w/v) solution), and methylol-melamine (1, 3, 6%(w/v) solution). Twenty g of activated carbon (32—48 mesh) was impregnated with 50 ml of additive solution for 24 hr at room temperature, then collected by filtration with suction. Activated carbon impregnated with N-additive solution in a covered crucible was continuously heated up to 850° for 2 hr in an electric furnace, kept for 5 min at 850°, and then cooled to room temperature under a nitrogen gas stream.

Measurement of pH in an Aqueous Dispersion——The pH of an aqueous dispersion of N-CAC was obtained according to the method of the Japanese Industrial Standards.[2]

Specific Surface Area——Specific surface area of N-CAC was obtained by the use of BET adsorption apparatus (Quantasorb, Yuasa-Quantachrome).

Measurement of N Content——The N content of N-CAC was determined on a Yanagimoto CHN analytical apparatus (MT-2).

Procedure for Adsorption of Hydrogen Sulfide——Hydrogen sulfide gas was of certified reagent grade (Seitetsu Kagaku Co.) and its purity was indicated to be 99.9%. Adsorption isotherms of hydrogen sulfide on N-CAC were determined in an all-glass vacuum system similar to that described previously.[3] The adsorbent was dried at 110° for 1 hr at 1×10^{-3} Torr before use, and the decrease in the weight of adsorbent due to heating was corrected for. Equilibrium amounts adsorbed at pressures up to 500 Torr were measured by a gravimetric method by using a BET adsorption apparatus with a spring balance.

Results and Discussion

1. Preparation of N-CAC and Its Adsorption of Hydrogen Sulfide

Table I shows the physical properties of N–CAC prepared by the introduction of

TABLE I. Physical Properties of N-Containing Activated Carbon

No.	N-Containing additives	N content (%)	pH[a]	Specific surface area (m^2/g)
1	Non	0.87	6.5	949.6
2	1 M ammonium acetate	0.69	6.2	1133.1
3	2 M ammonium acetate	0.69	6.3	1067.7
4	3 M ammonium acetate	0.89	6.2	1124.4
5	1 M ammonium carbonate	0.41	6.5	1167.0
6	2 M ammonium carbonate	0.41	6.6	1207.6
7	3 M ammonium carbonate	0.43	6.7	1194.3
8	1 M urea	1.59	6.1	1109.0
9	2 M urea	1.04	6.2	1113.1
10	3 M urea	1.51	6.3	1046.2
11	1 M *n*-butylamine	0.74	6.4	1015.1
12	2 M *n*-butylamine	0.75	6.2	1000.5
13	3 M *n*-butylamine	1.00	6.2	992.7
14	6% (w/v) methylol-melamine-urea	2.10	6.3	1028.9
15	12% (w/v) methylol-melamine-urea	3.35	6.3	916.7
16	25% (w/v) methylol-melamine-urea	4.31	6.7	892.8
17	25% (w/v) methylol-urea	5.51	8.7	622.8
18	1% (w/v) methylol-melamine	3.15	6.7	959.7
19	3% (w/v) methylol-melamine	2.41	6.8	940.1
20	6% (w/v) methylol-melamine	1.79	6.7	1046.9

a) The pH value is the pH of an aqueous dispersion.

TABLE II. Specific Adsorption of Hydrogen Sulfide on N-Containing Activated Carbon at Different Equilibrium Pressures

No.	Specific adsorption of hydrogen sulfide (%)				
	50 Torr	100 Torr	200 Torr	400 Torr	500 Torr
1	100.0 (39.0)[a]	100.0 (58.0)[a]	100.0 (87.7)[a]	100.0 (127.0)[a]	100.0 (143.0)[a]
2	87.4	97.6	99.9	102.5	102.8
3	99.0	101.1	102.1	104.3	105.0
4	91.0	100.3	101.4	104.7	105.6
5	87.7	94.0	94.2	96.1	96.4
6	82.1	98.6	101.1	103.5	102.7
7	89.0	100.0	102.2	105.5	106.2
8	101.8	102.6	102.6	103.5	102.0
9	90.3	101.0	102.9	103.7	102.9
10	89.7	96.7	94.5	97.6	100.3
11	98.2	105.7	103.4	101.0	101.4
12	80.0	90.5	91.4	92.5	92.2
13	79.7	88.3	87.8	92.1	93.8
14	106.9	104.4	102.6	103.0	102.2
15	120.0	112.4	104.7	103.1	100.7
16	122.3	117.6	108.0	101.3	99.6
17	105.1	106.9	94.6	85.9	81.8
18	106.7	115.0	110.6	105.0	102.6
19	105.9	105.7	104.0	102.9	100.6
20	97.9	102.9	100.7	100.2	100.0

a) The values are the amounts of hydrogen sulfide adsorbed (mg/g) on raw activated carbon (No. 1).
The amounts adsorbed at different equilibrium pressures were obtained from the adsorption isotherms at 30°.

N-additives. The fact that the N contents of Nos. 2, 3, 5—7, 11, and 12 were smaller than that of raw activated carbon (No. 1) was considered to be a result of loss of nitrogen from N-CAC during the heating up to 850°. Large amounts of nitrogen were introduced into raw activated carbon by the use of such additives as methylol-melamine-urea, methylol-urea, and methylol-melamine. The pH values of aqueous dispersions of N-CAC (except No. 17) were roughly the same as that of No. 1. The specific surface area of N-CAC decreased with increase in the N content, that is, a negative correlation was observed between them ($r=-0.854$, $p<0.001$). In contrast to this result, the specific surface areas of activated carbon preparations used for adsorption of sulfur dioxide have been reported to become larger than that of fresh activated carbon.[4]

Table II shows the specific adsorption of hydrogen sulfide on N-CAC at different equilibrium pressures. The specific adsorption behavior of N-CAC up to 500 Torr was classified into four groups on the basis of that of the raw activated carbon. That is, the first and second groups were N-CACs with lower and higher specific adsorption than raw activated carbon, respectively, and the third and fourth groups were N-CACs with higher specific adsorption at low pressures up to *ca.* 100 Torr and with lower specific adsorption at 500 Torr than those of the raw activated carbon, and *vice versa*, respectively. Figure 1 shows typical adsorption isotherms of the third and the fourth groups and the adsorption isotherm of raw activated carbon.

In order to clarify the effect of N content in N-CAC on the specific adsorption of hydrogen sulfide, the relationship between the specific adsorption and N content was obtained as shown in Fig. 2. As the amount adsorbed at the same equilibrium pressure is a suitable measure of

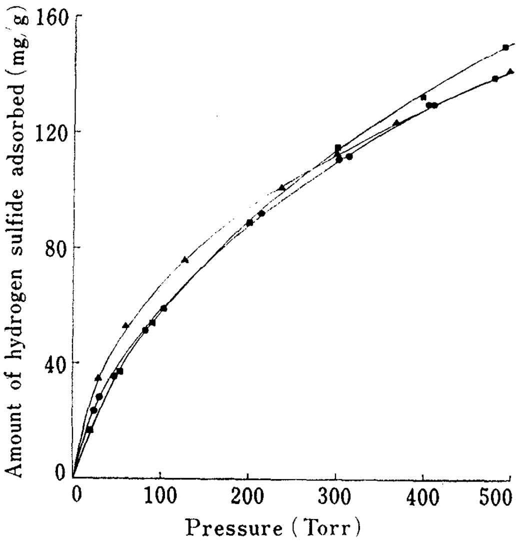

Fig. 1. Adsorption Isotherms of Hydrogen Sulfide on N-Containing Activated Carbon at 30°

●: No. 1, ■: No. 4, ▲: No. 16.

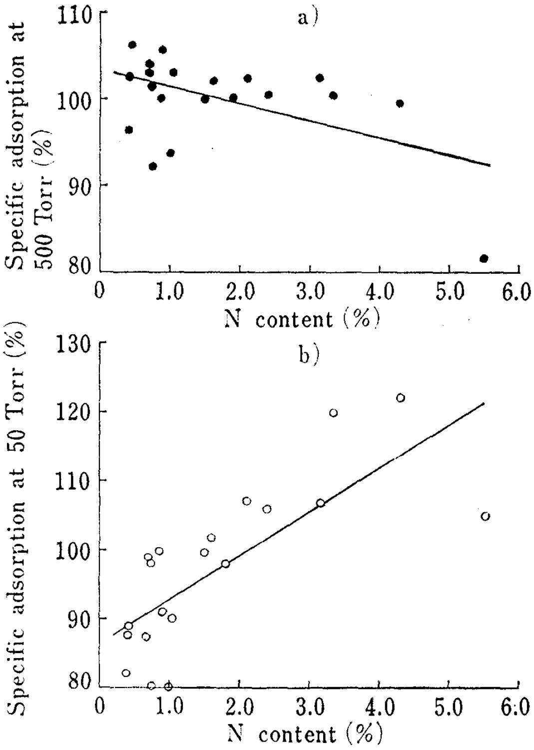

Fig. 2. Specific Adsorption of Hydrogen Sulfide *vs.* N Content of N-Containing Activated Carbon

a) Regression equation $Y=-1.979X+103.269$ ($r=-0.506$, $0.001<p<0.01$).

b) Regression equation $Y=6.407X+86.259$ ($r=0.755$, $p<0.001$).

the adsorption capacity of each adsorbent,[5] the amounts adsorbed on N–CAC at 50 and 500 Torr were obtained from the adsorption isotherms. The initial slopes between the amount adsorbed and pressure in the early stages up to *ca.* 50 Torr were steeper than the slopes in the range of *ca.* 50 to 500 Torr, as shown in Fig. 1. The amounts adsorbed at 50 and 500 Torr were set as the standards of amounts adsorbed at low and high pressure, respectively. Sano *et al.*[1b] reported that the amounts adsorbed on N–CAC were enhanced when nitrogen species were formed on raw activated carbon by the introduction of N-additives, but that they were not always proportional to N content. In the present work, a negative correlation between the specific adsorption at 500 Torr and N content, and a positive correlation between the specific adsorption at 50 Torr and N content were found, as shown in parts a) and b), respectively, of Fig. 2. It was concluded that N–CACs with large N content (Nos. 15 and 16) and N–CACs with small N content (Nos. 3, 4, and 7) were the preferred adsorbents for removing hydrogen sulfide at low and high pressure, respectively. Figure 3 shows the specific adsorption of hydrogen sulfide *vs.* specific surface area of N–CAC. A positive correlation between the specific adsorption at 500 Torr and specific surface area, and a negative correlation between the specific adsorption at 50 Torr and specific surface area were found, as shown in parts a) and b), respectively, of Fig. 3. The results indicate that the specific adsorption of hydrogen sulfide on N–CAC is dependent on the N content and specific surface area.

2. Thermodynamics of Adsorption of Hydrogen Sulfide in Pores of N-CAC

Dubinin and Astakhov[6] reported a thermodynamic equation for adsorption well suited to express the characteristics of gas adsorption by a porous adsorbent on the basis of the

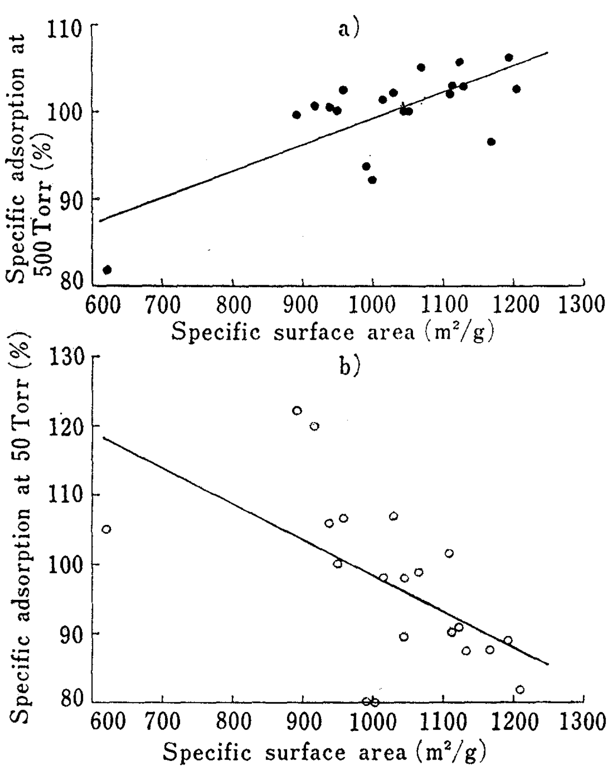

Fig. 3. Specific Adsorption of Hydrogen Sulfide *vs.* Specific Surface Area of N-Containing Activated Carbon

a) Regression equation $Y=0.030X+68.950$ ($r=0.721$, $p<0.001$).

b) Regression equation $Y=-0.051X+149.647$ ($r=-0.564$, $0.01<p<0.02$).

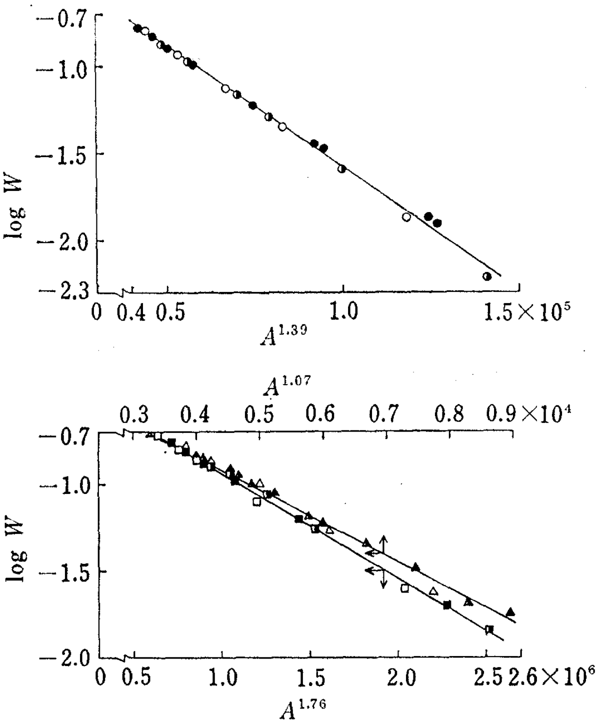

Fig. 4. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on N-Containing Activated Carbon

○: No. 1 at 20°, ●: No. 1 at 30°, ◑: No. 1 at 40°, □: No. 4 at 20°, ■: No. 4 at 30°, ◧: No. 4 at 40°, △: No. 16 at 20°, ▲: No. 16 at 30°, ◭: No. 16 at 40°,

W: the filled volume of the adsorption space. A: the decrease of free energy of adsorption.

potential theory of Polanyi.7)

$$W = W_0 \, exp[-(A/E)^n] \qquad (1)$$

$$A = \boldsymbol{R}T \ln(p_s/p) \qquad (2)$$

where W is the filled volume of the adsorption space. W_0 is the limiting volume of the adsorption space, A is the decrease of free energy of adsorption, E is the characteristic energy of adsorption at the characteristic point ($W/W_0=0.368$), n is a constant, $\boldsymbol{R}$ is the gas constant, T is the absolute temperature, p_s is the saturated vapor pressure, and p is the equilibrium pressure. The value of n can be determined by differentiating a plot of log V against A,8) where V is the volume of hydrogen sulfide gas (ml) adsorbed g^{-1} at STP. Figure 4 shows the application of the Dubinin–Astakhov equation to the adsorption isotherm on N–CACs (Nos. 1,4, and 16) at 20°, 30°, and 40°. Linear relationships were found between log W and A^n. Therefore, it appears that the adsorption of hydrogen sulfide on N–CAC resulted in the volume filling of micropores (pore radius<15Å).9) W_0 and E were estimated from the intercept at $A^n=0$ and the slope of the straight line was obtained by the least-squares method. The results obtained are shown in Table III. W_0 is the limiting adsorption value obtained when the whole adsorption space of micropores is filled by the adsorbed molecules.10) The fact that W_0 of No. 16 was larger than that of No. 1 indicates that the micropore volume was increased by impregnation with methylol-melamine-urea. The relationship between E and ΔH_0 (heat of condensation of hydrogen sulfide, 4.46 kcal/mol11)) has been reported to be $E \fallingdotseq 1/3\ \Delta H_0$ at $n=1$ and $E \fallingdotseq 2/3\ \Delta H_0$ at $n=2$.12) In this study, the relationship between E and ΔH_0 of Nos. 1 and 16 was also found to be $E \fallingdotseq 1/3\ \Delta H_0$ at $n \fallingdotseq 1$, and that between E and ΔH_0 of No. 4 was found to be $E \fallingdotseq 2/3\ \Delta H_0$ at $n \fallingdotseq 2$. The fact that the smaller W_0, the larger was the n value indicates that the smaller the micropore volume, the larger was the decrease in the degree of freedom of hydrogen sulfide, in molecular translation ,due to adsorption.12)

TABLE III. Limiting Volume of Adsorption Space, Characteristic Energy of Adsorption, and n Value of the Dubinin–Astakhov Equation

No.	W_0 (ml/g)	E (cal/mol)	n
1	0.6545	1705	1.39
4	0.4711	2116	1.76
16	0.8164	1378	1.07

The isosteric heat of adsorption was calculated from the adsorption isotherms at three different temperatures, 20°, 30°, and 40°. The isosteric heats of adsorption of Nos. 1, 4, and 16 were 7.98—7.09, 8.45—5.85, and 8.33—6.35 kcal/mol, respectively, in the ranges of W/W_0 0.03—0.30. Since their isosteric heats of adsorption were less than twice the value of ΔH_0, hydrogen sulfide seems to be physisorbed in this range according to Jones and Ross' definition.13)

According to Dubinin,10) it is possible to write the following expressions for the net differential heat of adsorption q and for the differential molar entropy of adsorption ΔS,

$$q = E[(\ln a_0/a)^{\frac{1}{n}} + \alpha T/n(\ln a_0/a)^{\frac{1}{n}-1}] \qquad (3)$$

$$\Delta S = -\alpha E/n(\ln a_0/a)^{\frac{1}{n}-1} \qquad (4)$$

where a_0 is the limiting amount adsorbed (mmol/g), a is the amount adsorbed, and α is the coefficient of thermal expansion of the adsorbate. Figure 5 shows the dependence of q of hydrogen sulfide on N–CAC upon the degree of filling of micropores θ ($=a/a_0$). In all cases, q decreased with increasing θ value. The results indicated that the micropores of N–CAC (Nos. 1, 4, and 16) were successively filled from the smallest pores to pores of large dimensions.[14] The continuous decrease of q with increase in θ value indicates the energy heterogeneity of the volume of the adsorption space of micropores.

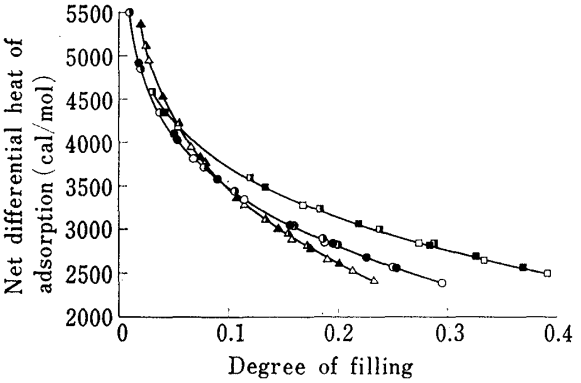

Fig. 5. Dependence of Net Differential Heat of Adsorption of Hydrogen Sulfide on N-Containing Activated Carbon upon the Degree of Filling

○: No. 1 at 20°, ●: No. 1 at 30°, ◑: No. 1 at 40°, □: No. 4 at 20°, ■: No. 4 at 30°, ◨: No. 4 at 40°, △: No. 16 at 20°, ▲: No. 16 at 30°, ◭: No. 16 at 40°.

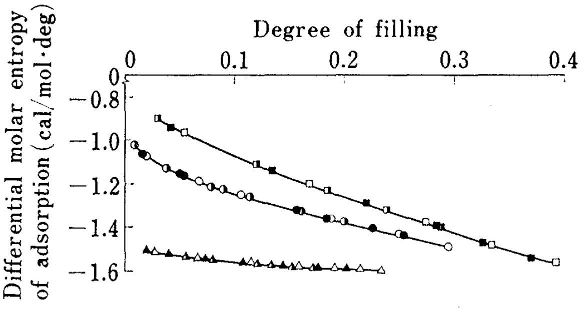

Fig. 6. Dependence of Differential Molar Entropy of Adsorption of Hydrogen Sulfide on N-Containing Activated Carbon upon the Degree of Filling

○: No. 1 at 20°, ●: No. 1 at 30°, ◑: No. 1 at 40°, □: No. 4 at 20°, ■: No. 4 at 30°, ◨: No. 4 at 40°, △: No. 16 at 20°, ▲: No. 16 at 30°, ◭: No. 16 at 40°.

The value of q of No. 16 was larger than that of No. 1 at θ values below 0.09 whereas it was smaller than that of the latter at θ values above 0.09. The larger the pore volume, the larger is the amount adsorbed at the same θ value, and the larger the amount adsorbed, the larger is q. Accordingly, q is closely related to the pore volume. The results obtained indicate that the micropore volume of No. 16 is larger than that of No. 1 at less than a certain radius, whereas at higher radii, the situation is reversed. Figure 6 shows the dependence of ΔS of hydrogen sulfide on N–CAC upon θ value. ΔS became smaller with increase in θ value. The results obtained suggest that the hydrogen sulfide molecules are compactly filled in the micropores at the early stage of filling, that is, in the pores of smaller dimensions. It is considered that when the dependence of ΔS upon θ value is still small, the degree of compactness of hydrogen sulfide filled in micropores is roughly the same. Therefore, hydrogen sulfide filled in micropores of No. 16 may have the same compactness in this range of θ value. The fact that ΔS of No. 16 was smaller than that of No. 1 was consistent with the result that the n value ($n=1.07$) of No. 16 was smaller than that ($n=1.39$) of No. 1. The differential molar entropy change became smaller with increase in the degree of filling. This entropy change indicates that the properties of hydrogen sulfide in the adsorbed state are different from those of liquid hydrogen sulfide.

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