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Steric Effect in the Adsorption of Ammonia and Trimethylamine into Micropores of Activated Carbon

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The difference in adsorption behavior of ammonia and trimethylamine on carbon was investigated on the basis of the Dubinin–Radushkevich plots and the $-dW/d(A/\beta)$ distributions. The micropore size was heterogeneous to ammonia, whereas it was homogeneous to trimethylamine. Ammonia and trimethylamine were adsorbed selectively into the small micropores and the large micropores, respectively. The ratios of the average values of pore diameter to the molecular size for ammonia and trimethylamine were approximately constant, being from 1.8 to 2.4. N-Containing activated carbon characteristically showed a larger adsorption capacity for a polar adsorbate of small size, such as ammonia or hydrogen sulfide, than did raw activated carbon.

Keywords——ammonia; trimethylamine; micropore; N-containing activated carbon; Dubinin–Radushkevich plot; adsorption volume distribution; adsorption potential; steric effect

Introduction

Ammonia and trimethylamine, which are often discharged into the atmosphere from carcass processing plants, sewage treatment plants, *etc.*, have a noxious odor and are toxic. Thus, it is desirable to investigate the adsorption characteristics of ammonia and trimethylamine on activated carbon in order to remove them effectively by means of an adsorption method.

Adsorption in fine pores is dependent on the ratio of the pore size (D) to the molecular diameter of the adsorbate (d) rather than the pore size itself.[1] Everett and Powl[2] calculated theoretically the relationship between the enhancement of interaction potential and the ratio of the pore radius to the collision radius of adsorbate. Kawazoe *et al.*[3] showed that D/d was related to the parameter n included in the Dubinin–Radushkevich (D–R) equation. According to Suzuki and Sakoda,[4] both parameters n and E (characteristic energy of adsorption) involved in the D–R equation can be assumed to vary with D/d.

The purpose of this paper is to elucidate the characteristics of adsorption of ammonia and trimethylamine into the micropores of carbon on the basis of thermodynamic data such as the D–R plots of adsorption isotherms and the $-dW/d(A/\beta)$ distributions. Moreover, the adsorption characteristics of N-containing activated carbon (N-CAC) are discussed on the basis of the adsorption isotherms of ammonia and trimethylamine.

Experimental

Materials——Ammonia gas was of certified grade from Seitetsu Kagaku Co. and its purity was indicated to be

99.9%. Trimethylamine gas with a purity of better than 99.0% was obtained from Matheson Gas Products. Activated carbon No. 1 was obtained commercially from Wako Pure Chemical Ind., Ltd. Activated carbon No. 2 was N-CAC prepared by impregnating activated carbon No. 1 with 25% methylol melamine urea alcohol solution.[5] The particle sizes of these adsorbents were 32—48 mesh. The specific surface area of activated carbon was measured with a BET apparatus by using nitrogen gas at liquid nitrogen temperature; the procedure for measurement of pore volume was described previously.[6]

Procedure for Adsorption——Adsorption isotherms of ammonia and trimethylamine on activated carbon were determined in an all-glass vacuum system similar to that described previously.[7] The equilibrium amounts adsorbed at pressures up to 600 Torr were measured at 30 °C by a gravimetric method by using a BET apparatus with a spring balance.

Results and Discussion

Type of Adsorption Isotherm of Ammonia and Trimethylamine

Table I lists the physical properties of the carbons used. Specific surface area and micropore volume of N-CAC (No. 2) were decreased by 16—17% as compared with raw activated carbon (No. 1).

Figures 1 and 2 show the adsorption isotherms of ammonia and trimethylamine, respectively. A remarkable difference in the type of adsorption isotherm of ammonia and trimethylamine was observed in the range of less than 600 Torr. The types of adsorption isotherms of ammonia and trimethylamine in this range of pressure resemble type III and type I, respectively in the classification of Brunauer, Deming, Deming, and Teller.[8] The molecular dimensions of ammonia and trimethylamine are 3.7 and 5.9 Å, respectively.[9] These results indicate that the types of adsorption isotherms on the same carbon are seriously affected by the molecular size of the adsorbates, that is, the ratio of the pore size of the adsorbent to the molecular size of the adsorbate.

The adsorption capacity of N-CAC (No. 2) for ammonia is larger than that of raw

Table I. Physical Properties of Carbon Samples Used

Activated carbon No.	Specific surface area (m^2/g)	Micropore volume (ml/g)	N-Content (%)
1	1013.2	0.425	0.87
2	854.9	0.354	4.31

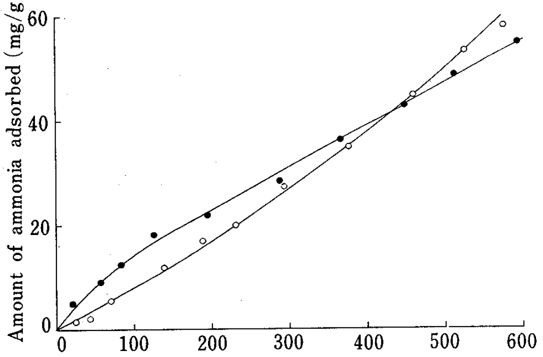

Fig. 1. Adsorption Isotherms of Ammonia on Carbon

○, raw activated carbon; ●, N-CAC.

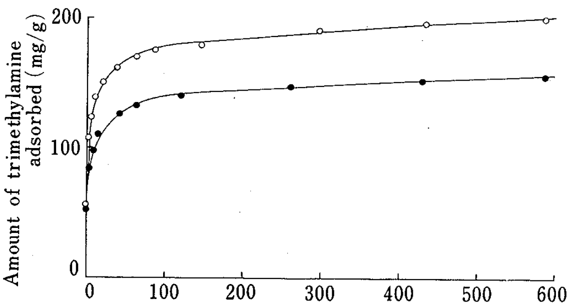

Fig. 2. Adsorption Isotherms of Trimethylamine on Carbon

○, raw activated carbon; ●, N-CAC.

activated carbon. This tendency was the same as that in the case of hydrogen sulfide.[5] However, the adsorption capacities of N-CAC and raw activated carbon for trimethylamine are reversed, as shown in Fig. 2. It can be concluded that the N-CAC is a characteristic adsorbent whose adsorption capacity for a polar adsorbate of small size, such as ammonia or hydrogen sulfide, is larger than that of the raw activated carbon.

Steric Effect of Adsorption of Ammonia and Trimethylamine

Dubinin and Radushkevich[10] proposed the following (D–R) equation for adsorption in microporous carbon,

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(P_s/P)] \qquad (1)$$

where W is the volume adsorbed at a relative pressure P/P_s, W_0 is the limiting volume of the adsorption space, B is the structural constant, T is the absolute temperature, and β is the similarity coefficient.

Figure 3 shows the D–R plots for adsorption of ammonia and trimethylamine on carbon at 30 °C. Large positive deviations and small negative deviations from the D–R plots for ammonia and trimethylamine, respectively, were observed at high pressures. The types of D–R plots of ammonia and trimethylamine roughly corresponded to type B and type A, respectively, in the classification of Rand.[11] Rand[11] noted that the type A deviation in D–R plots was often found for adsorption in microporous zeolites which have discrete micropore sizes rather than a distribution of micropore sizes, that is, such plots were typical of adsorption onto a nearly homogeneous surface. However, it is impossible to conclude that an adsorbent showing type A in D–R plots has an essentially uniform pore size, like zeolite, because a difference in the type of D–R plot for the adsorption of ammonia and trimethylamine on the same carbon was observed as shown in Fig. 3. This result indicates that the micropore size of the carbon used here is uniform for a large adsorbate, such as trimethylamine, whereas it is not necessarily uniform for a small adsorbate such as ammonia.

The inertia radius R_i and the characteristic size x of micropores can be expressed[12] as $R_i = \sqrt{62B \times 10^6}$ and $x = 0.878R_i$, respectively. The structural constant (B) was calculated from the slopes of the straight lines of the D–R plots. Table II shows the values of B, R_i, and x obtained from the adsorption data. The characteristic size of micropores x is an average value

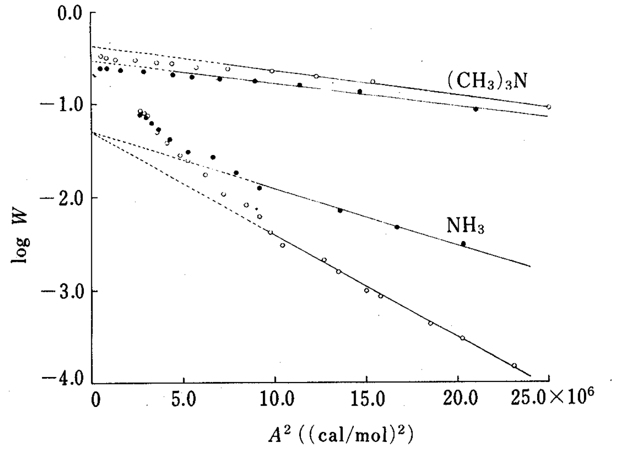

Fig. 3. Dubinin–Radushkevich Plots of Adsorption Isotherms of Ammonia and Trimethylamine on Carbon

W, the volume of amount adsorbed (ml/g); A, the decrease of free energy of adsorption; ○, raw activated carbon; ●, N-CAC.

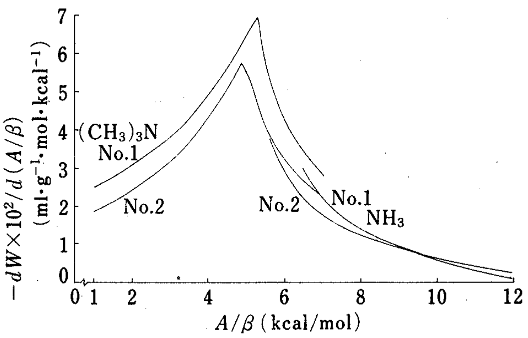

Fig. 4. Comparison of Distributions of W with A/β for the Adsorptions of Ammonia and Trimethylamine

Table II. Values of Structural Constant, Inertia Radius, and Characteristic Size of Micropores

Activated carbon No.	Ammonia			Trimethylamine		
	$B\times10^6$ (K^{-2})	R_i (Å)	x (Å)	$B\times10^6$ (K^{-2})	R_i (Å)	x (Å)
1	0.42	5.1	4.5	0.88	7.4	6.5
2	0.22	3.7	3.3	0.87	7.4	6.5

of radii which corresponds to the characteristic point of the adsorption isotherm.[12] The fact that x for ammonia was smaller than x for trimethylamine by about 2—3 Å indicates that ammonia and trimethylamine are selectively adsorbed in smaller micropores and in larger ones, respectively. According to Everett and Powl,[2] enhancement of interaction potential in a slit-shaped pore or a cylindrical pore is still appreciable when the pore radius is 1.5 or 2.5 times, respectively, the radius of the adsorbate. Since the molecular dimensions of ammonia and trimethylamine are 3.7 and 5.9 Å,[9] respectively, the ratio of x to the radius of ammonia molecule was 1.8—2.4 and the ratio of x to the radius of trimethylamine was 2.20. Our results agree approximately with the values calculated by Everett and Powl.[2]

By substituting the equation $A=\boldsymbol{R}T\ln(P_s/P)$ into the D–R equation and differentiating the equation $\ln W=\ln W_0-(A/\beta E)^2$ in the logarithmic form, we obtain

$$-dW/d(A/\beta)=2W_0A/\beta E^2\exp[-(A/\beta E)^2] \qquad (2)$$

Equation (2) has the form of a Rayleigh distribution. Figure 4 compares the distributions of W with A/β for the adsorption of ammonia and trimethylamine. Experimental $-dW/d(A/\beta)$ distributions were obtained by the differentiation of the characteristic curves of W *vs.* A/β in the range of pressures up to 600 Torr. The distributions for different adsorbates, ammonia and trimethylamine, have been corrected by use of the similarity coefficient β.

The relations of $-dW/d(A/\beta)$ with A/β for adsorption of ammonia and trimethylamine show uneven distribution in the high range of A/β and the low range of A/β, respectively. This result indicates that ammonia and trimethylamine are adsorbed selectively into the small micropores and the large micropores, respectively. The forms of distribution of ammonia and trimethylamine are clearly very different. A Rayleigh distribution for the adsorption of ammonia could not be observed in this range of A/β, whereas a Rayleigh distribution was present for the adsorption of trimethylamine. The $-dW/d(A/\beta)$ distribution is an approximate measure of the energetic heterogeneity of the pore surface.[13] The results indicate that adsorption of ammonia into the small micropores is more heterogeneous than that of trimethylamine into the large micropores.

It has been pointed out that there are qualitative relations between changes in $-dW/d(A/\beta)$ distributions and micropore size distribution of the adsorbent when the same adsorbate is used.[14] Hence, the above interpretation of the form of the distribution is consistent with the discussion of the results of the D–R plots.

The amounts of ammonia adsorbed on N-CAC (No. 2) at low pressure (Fig. 1) and the values of $-dW/d(A/\beta)$ at high A/β (Fig. 4) are greater than for the raw activated carbon (No. 1), showing that introduction of nitrogen increased the adsorption capacity for ammonia and widened the size distribution of small micropores. This conclusion suggests that there have been increases in the capacity and the size distribution of the smallest pores, possibly because nitrogen introduction creates new small pores rather than enlarging existing small pores.

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