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Adsorption of Various Kinds of Offensive Odor Substances on Activated Carbon and Zeolite

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Ammonia, methanethiol, hydrogen sulfide, methyl sulfide, trimethylamine, acetaldehyde, styrene, and methyl disulfide are listed as the offensive odor substances by the Offensive Odor Control Law in Japan. We have reported on the mechanism of adsorption of these substances by solid adsorbents (MIYOSHI et al. 1976, 1977ab, 1978ab; TANADA 1977; TANADA & BOKI 1974, 1978a; TANADA et al. 1978abc).

The purpose of this work was to find a useful correlation for estimating the adsorptive capacity of these offensive odor substances on porous adsorbents. Relation between the amount of gases adsorbed (mL/g) on wood charcoal and their boiling points, van der Waals constants, and heat of vaporization was discussed (YANAI & KANO 1972). GRANT et al. (1962) presented a correlation for estimating the adsorptive capacity of sulfur compounds (methanethiol, ethanethiol, propanethiol, hydrogen sulfide, carbonyl sulfide, and carbon disulfide) on activated carbon. Here, the relation between the amount of offensive odor substances sorbed on adsorbent (activated carbon and zeolite) and their cross-sectional areas is discussed.

EXPERIMENTAL

Materials: Ammonia, hydrogen sulfide, and methyl sulfide were obtained from Seitetsu Kagaku Company, and their labeled purities were 99.9%, 99.9%, and 98.0%, respectively. Methanethiol and trimethylamine of 99.07% purity were obtained from Matheson Gas Products, U.S.A. Methyl sulfide, acetaldehyde, and styrene, commercially purified material, were purified by vacuum distillation. Activated carbon and zeolite used were commercial products. The particle size of adsorbents were 200-400 mesh.

Procedure of Adsorption: The adsorbent was dried at 110°C for 1 h at 1×10^{-2} Torr before use. Equilibrium amount adsorbed was measured by a gravimetric method using a B.E.T. apparatus with a spring balance at 30°C.

Measurement of Pore Size Distribution: For the four kinds of adsorbents the pore size distribution in the range of 7.5 to 300 Å was obtained by the method of DOLLIMORE & HEAL (1964).

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Surface pH and Specific Surface Area: Surface pH values of zeolite were obtained with a Nishicator (Nishio Universal Indicator). The method of measuring the pH of activated carbon was as given by URANO et al. (1976). The specific surface area of adsorbent was measured with a B.E.T. apparatus using argon gas as an adsorbate at liquid nitrogen temperature.

Calculation of Cross-sectional Area of Molecules: The numerical value of cross-sectional area of a molecule was calculated by using the following equation (EMMETT & BRUNAUER 1937) : $S = 3.464(M/4\sqrt{2}N_A\rho)^{2/3}$, where M is the molecular weight of an adsorbate, N_A the Avogadro number, and ρ the adsorbate density in the liquid state. Derivation of this equation is based on the assumptions concerning the arrangement of molecules in the adsorbed layer (a hexagonal, close-packed lattice).

RESULTS AND DISCUSSION

The concentration of eight offensive odor substances is limited in Japan as listed in Table 1. Adsorption of these gases was measured in order to remove them by using activated carbon and zeolite. The amount adsorbed is one of the parameters required in choosing a suitable adsorbent for practical use, and it is considered to be mainly determined by physical properties of the gases and physicochemical properties of the adsorbents. Table 1 shows the physical properties of offensive odor substances.

Parallelism between the amount of gases adsorbed (mL/g) on wood charcoal and boiling points of 14 kinds of gases has been discussed (YANAI & KANO 1972). Their boiling points were below -7 °C and they therefore are in a gaseous state at room temperature. Their cross-sectional areas were almost equal and smaller than those of the offensive odor substances listed in Table 1. Several of the offensive odor substances in Table 1 are in gaseous state and others are in liquid state at room temperature, and their cross-sectional areas are in a wide range from about 11 to 36 $\mathring{A}^2$.

The amount adsorbed (mmol/g) on the four kinds of adsorbents is shown in Table 2. The amounts adsorbed at a certain relative pressure ($p_e/p_s = 0.006$) were obtained from their adsorption isotherms in order to compare the amounts adsorbed at the same state of adsorption for eight kinds of offensive odor substances on activated carbon and zeolite. No relationship could be found between the amount of offensive odor substances adsorbed on activated carbon and zeolite, and the boiling points of these substances.

GRANT et al. (1962) presented a useful correlation for estimating the adsorptive capacity of chemically similar sulfur compounds (mercaptan, hydrogen sulfide, carbonyl sulfide, and carbon disulfide) from their

TABLE 1

Physical Properties of Offensive Odor Substances

Offensive Odor Substance	Formula	Boiling Point (°C)	Olfactory Threshold (ppm) a)	Concentration Limit of Regulation (ppm)	Vapore Pressure at 30°C (Torr)	Cross-sectional Area (Å²)
Ammonia	NH_3	-33.4	0.037	1 -5	8664	13.0, 11.7d) 14.6,d) 14.8e)
Methanethiol	CH_3SH	6.1	0.0011	0.002 -0.01	1771	22.3
Hydrogen Sulfide	H_2S	-60.1	0.0011	0.02 -0.2	16918	16.5, 21.0f)
Methyl Sulfide	$(CH_3)_2S$	38.0	0.02	0.01 -0.2	580	26.8
Trimethylamine	$(CH_3)_3N$	3.2	0.4	0.005 -0.07	1976	30.3
Acetaldehyde	CH_3CHO	20.2	0.066b)	0.05 -0.5	1143	22.2
Styrene	$C_6H_5-CH=CH_2$	145.5	0.04 c)	0.4 -2	10	36.1
Methyl Disulfide	$(CH_3)_2S_2$	109.7	0.015c)	0.009 -0.1	36	30.4

a) SUMMER, W.: Methods of Air Deodorization, London, Elsevier Publishing Co., 1963.
b) Osmic threshold, ibid.
c) Estimate.
d) KUBO, T., E. SUITO, U. NAKAGAWA, and S. HAYAKAWA (Eds.).: Funtai, Riron to Oyo, Tokyo, Maruzen, 1962.
e) HAYAKAWA, S. (Ed.).: Funtai Bussei Sokuteiho, Tokyo, Asakura, 1973.
f) HARRIS, B.L. and P.H. EMMETT: J. Phys. Chem. 53, 811 (1949).

TABLE 2

Amount of Offensive Odor Substances Adsorbed on Adsorbents

Adsorbent	Amount Adsorbed (mmol/g)							
	NH_3	CH_3SH	H_2S	$(CH_3)_2S$	$(CH_3)_3N$	CH_3CHO	$C_6H_5-CH=CH_2$	$(CH_3)_2S_2$
Activated Carbon No.1	0.567	2.318	1.467	2.575	2.453	1.862	2.433	3.100
Activated Carbon No.2	0.446	2.083	1.351	2.733	2.952	2.872	2.965	3.200
Zeolite No.3	4.568	2.058	2.210	1.986	1.765	2.990	0.394	1.285
Zeolite No.4	5.109	1.758	3.908	2.277	1.540	3.274	0.500	1.765

Amount adsorbed was measured at 30 °C and $p_e/p_s = 0.006$.

adsorption isotherms. The offensive odor substances in Table 1 however are chemically different compounds, that is, some are sulfur compounds and the other are nitrogen compounds. The correlation (GRANT et al.1962) of adsorption results required data on the vapor pressure, fugacity, and liquid density of adsorbate over a wide range of conditions. It is preferable to obtain the correlation which adsorptive capacities of chemically different odor substances can be expressed simply with their physical properties.

TABLE 3

Physicochemical Properties of Adsorbents

Adsorbent	Surface pH	Surface Area (m^2/g)	Micropore Volume (mL/g)	Transitional Pore Volume (mL/g)
Activated Carbon No.1	7.0	1209.0	0.3924	0.1643
Activated Carbon No.2	11.0	495.0	0.2300	0.1966
Zeolite No.3	8.6	525.6	0.1532	0.0704
Zeolite No.4	6.0	352.6	0.1921	0.0576

Table 3 shows the physicochemical properties of adsorbents used. The surface pH of activated carbon and zeolite except No.4 was on the alkaline side. The data indicated that the amount adsorbed on them was hardly affected by their surface pHs. Activated carbon No.1 with the largest surface area did not always show the largest amount adsorbed. The pore structure of adsorbent is customarily divided into three classes, micropores (radius < 15-16 Å), transitional pores (15-16 Å < radius < 1000-2000 Å), and macropores (radius > 1000-2000 Å) (DUBININ 1966). The fact that micropore volumes of activated carbon and zeolite were larger than their transitional pore volumes indicated that the adsorbents used were mainly occupied by micropores. Figure 1 shows the pore size distribution curves of adsorbents. The pore size distribution curves of activated carbon had maxima at radius 7.5 Å and the differential pore volumes of zeolite were larger than those of activated carbon at radius 6.5 Å. This result showed that the pore radii of zeolite were smaller than those of activated carbon.

Figures 2 and 3 show the amount adsorbed on activated carbon and zeolite, respectively, vs. cross-sectional areas of eight kinds of offensive odor substances. Amount of offensive odor substances adsorbed on activated carbon increased with increasing cross-sectional area up to about 22 $Å^2$, and then it was constant in the range of 22 to 36 $Å^2$. However, the amount adsorbed on zeolite decreased with an increase in cross-sectional area of the offensive odor substances. These offensive odor substances are classified into two groups; one having a smaller cross-sectional area

(NH_3 and H_2S) and the other having a larger area (CH_3SH, $(CH_3)_2S$, $(CH_3)_3N$, CH_3CHO, $C_6H_5-CH=CH_2$, and $(CH_3)_2S_2$). Results in Figs. 2 and 3 indicated that zeolite was more suitable for removing offensive odor substances with smaller cross-sectional area of about 20 $Å^2$, and that activated carbon was a suitable adsorbent for removing other substances with cross-sectional area larger than about 22 $Å^2$. According to the theory of London-van der Waals force (LONDON 1930), adsorption in the smallest pores of an adsorbent into which an adsorbate can enter is considered more preferable than that on its plane surfaces. The pore diameter of commercial zeolite used is normalized to 9 Å (No.3) and 10 Å (No.4). The fact that adsorption of ammonia and hydrogen sulfide with smaller cross-sectional area of about 20 $Å^2$ on zeolite was more preferable than that on activated carbon can be well explained by the theory of London-van der Waals force and by the fact that pore volumes of zeolite were larger than those of

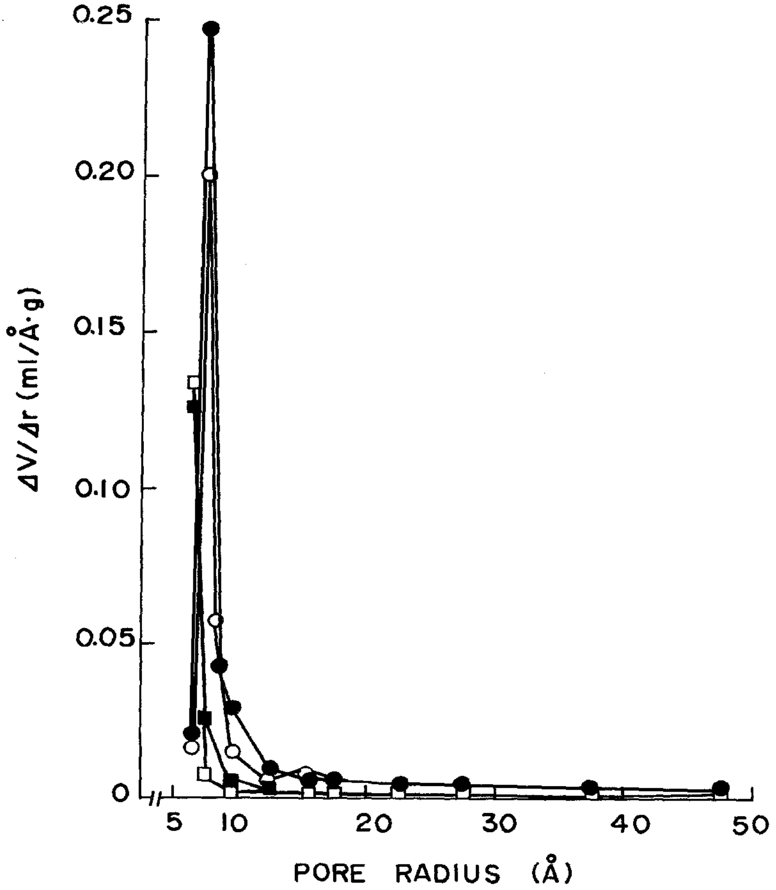

Fig. 1. Pore Size Distribution Curves of Adsorbents. Activated Carbon No.1 ● , Activated Carbon No.2 ○ , Zeolite No.3 ■ , and Zeolite No.4 □

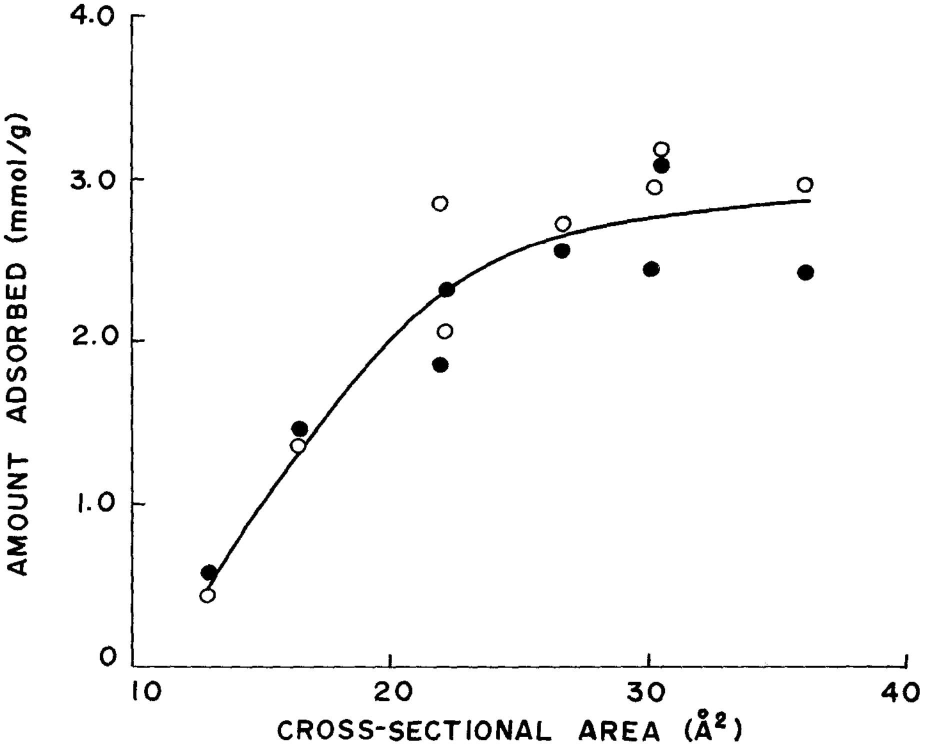

Fig. 2. Amount Adsorbed on Activated Carbon vs. Cross-sectional Area of Offensive Odor Substances. Activated Carbon No.1 ● ,Activated Carbon No.2 ○

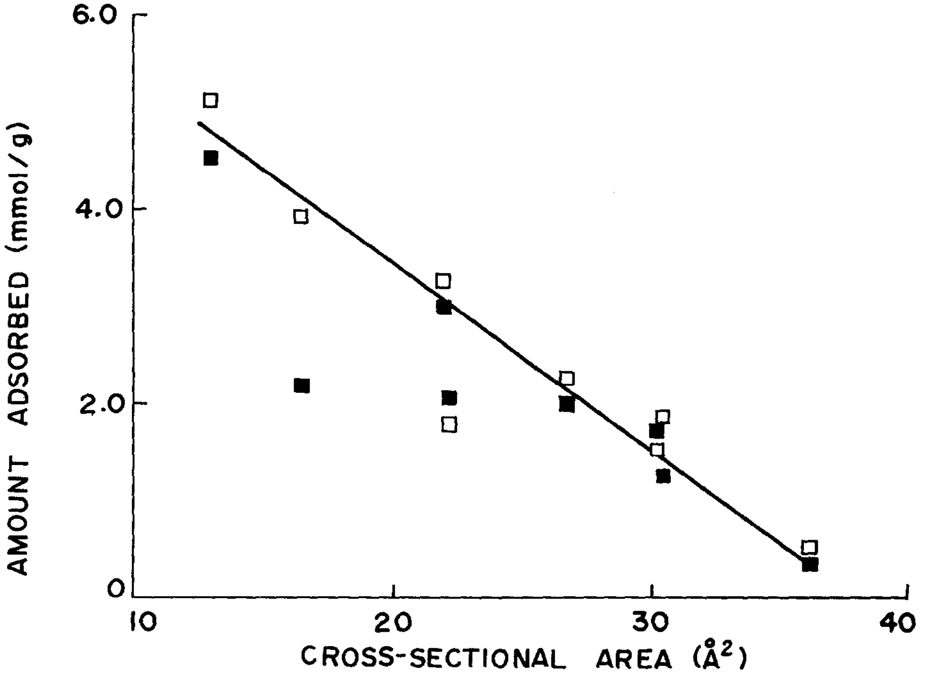

Fig. 3. Amount Adsorbed on Zeolite vs. Cross-sectional Area of Offensive Odor Substances.
Zeolite No.3 ■ , Zeolite No.4 □

activated carbon at radius 6.5 Å(Fig. 1). From the results of Figs. 2 and 3, it is considered that the offensive odor substances with smaller cross-sectional area of about 20 $Å^2$ such as ammonia and hydrogen sulfide was preferably adsorbed on the adsorbent whose pore volume below radius 6.5 Å was rich.

The purpose of this work was to find a useful correlation for estimating the adsorptive capacity of offensive odor substance on porous activated carbon and zeolite. We found such a correlation between the amount adsorbed on them and cross-sectional area of adsorbate molecule. The cross-sectional area of offensive odor substance can easily be calculated from the equation $s = 3.464(M/4\sqrt{2}\ N_A \rho)^{2/3}$. The adsorptive capacities of offensive odor substances unlimited on porous activated carbon and zeolite can easily be estimated from the relation curves represented in Figs. 2 and 3.

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