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Adsorption Behavior of Hydrogen Sulfide Inside Micropores of Molecular Sieve Carbon 5A and Molecular Sieve Zeolite 5A

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Hydrogen sulfide has a noxious odor and is toxic. Several studies on adsorption of hydrogen sulfide onto zeolite (HELLMUT & JANOS 1978, ROBERT et al.1979), silica gel(JONES & ROSS 1968), alumina(CHRISTIAN & JACK 1979), and activated carbon(BOKI & TANADA 1980) have been reported. The primary interest in these studies was in relation to the reversibility of hydrogen sulfide adsorption onto these adsorbents.

This study was made on the adsorption behavior inside the micropores of Molecular Sieve Carbon 5A (MSC-5A) and Molecular Sieve Zeolite 5A (MSZ-5A), where such a fundamental investigation is useful from the viewpoint of their practical use for the selective adsorption and catalytic decomposition of the offensive odor substances. The adsorption behavior was discussed on the basis of the adsorption isotherms and the thermodynamic data.

EXPERIMENTAL

Materials: Hydrogen sulfide gas was of certified reagent grade (Seitetsu Kagaku Co.), and its purity was indicated to be 99.9%. The adsorbents were commercial products; MSC-5A (Takeda Seiyaku Co.) and MSZ-5A (Nippon Kuromato Kogyo Co.), and their physical properties are given in Table 1.

Procedure for Adsorption: The adsorbent was dried at 110 C for 1 h at 1×10^{-2} Torr before use. Equilibrium amounts adsorbed at pressures up to 500 Torr were measured by a gravimetric method using a B.E.T. apparatus with a spring balance at 20 and 30 C.

RESULTS AND DISCUSSION

1. Adsorption of Hydrogen Sulfide on MSC-5A and MSZ-5A. Figure 1 shows adsorption isotherms of hydrogen sulfide on MSC-5A and MSZ-5A at 20 and 30 C. The adsorption isotherm of MSC-5A was dissimilar in form to that of MSZ-5A. The adsorption isotherm of MSC-5A rose gradually up to 500 Torr. However, the adsorption isotherm of MSZ-5A rose sharply at about 100 Torr and then

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reached a plateau. The amounts of hydrogen sulfide adsorbed on MSZ-5A up to about 150 Torr were larger than those on MSC-5A. It was concluded that MSC-5A and MSZ-5A were the preferred adsorbent for removing hydrogen sulfide in the ranges of high and low pressure, respectively. MSZ-5A yielded the adsorption isotherm with a sharper knee, i.e. showed a higher adsorption in the low pressure range, than did MSC-5A. According to the

Table 1. Properties of Adsorbent Used

Adsorbent	Surface Area[a) (m^2/g)	pH[b)	Pore Volume[c) (mL/g)	Particle Size (mesh)
MSC-5A	485.7	5.8	0.0295	4 - 7
MSZ-5A	264.4	6.0	0.0423	1 - 8

a) By argon B.E.T. method.

b) The pH of MSC-5A was measured by the method of HAGIWARA et al.(1973), and pH of MSZ-5A was measured using Nishicator (Nishio Universal Indicator;Nishio Kogyo Co., Ltd., Tokyo, Japan).

c) By the method of BENESI et al. (1955).

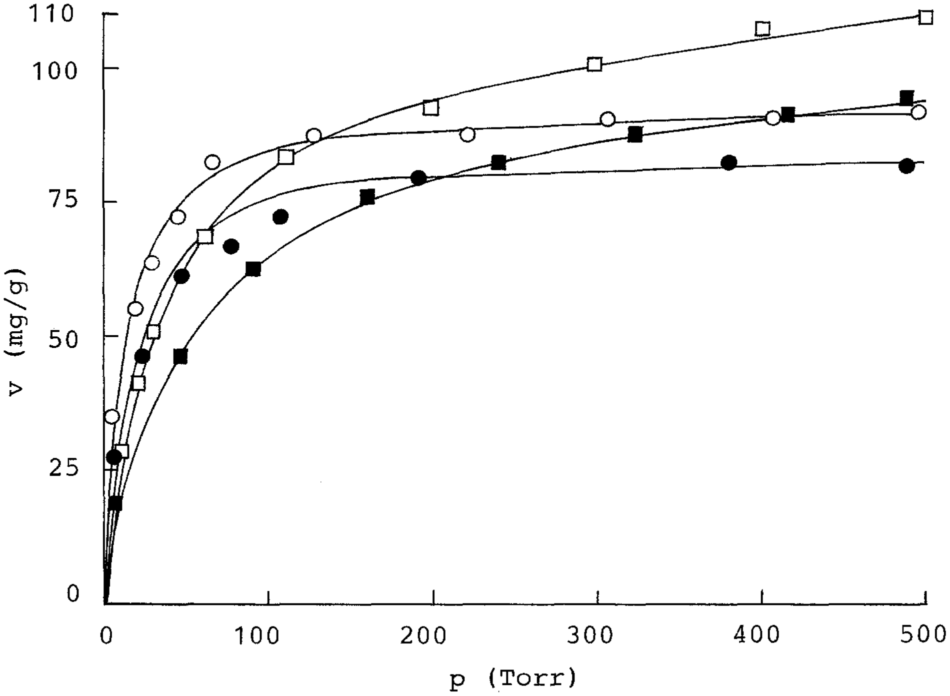

Fig. 1. Adsorption Isotherms of Hydrogen Sulfide on MSC-5A and MSZ-5A. Square symbols and circle symbols denote the experimental data of MSC-5A and MSZ-5A, respectively. v: amount of hydrogen sulfide adsorbed; p: equilibrium pressure; □, ○ : 20 C; ■, ●: 30 C.

view of GREGG & SING (1967), it is possible to conclude from the result given above that the pore size distribution of MSZ-5A is displaced towards the fine pores as compared with that of MSC-5A.

2. Thermodynamics of Adsorption of Hydrogen Sulfide on MSC-5A and MSZ-5A.

DUBININ & ASTAKHOV (1971) reported a thermodynamic equation for adsorption well suited to express the characteristics of gas adsorption by a porous adsorbent on the basis of the potential theory of POLANYI (1914),

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

$$A = RT \ln(p_s/p) \qquad (2)$$

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, R is the gas constant, T is the absolute temperature, p_s is the saturated vapor pressure, and p is the equilibrium pressure. Figure 2 shows the application of the Dubinin-Astakhov equation to the adsorption isotherms on MSC-5A and MSZ-5A at 20 and 30 C. Linear relationships were found

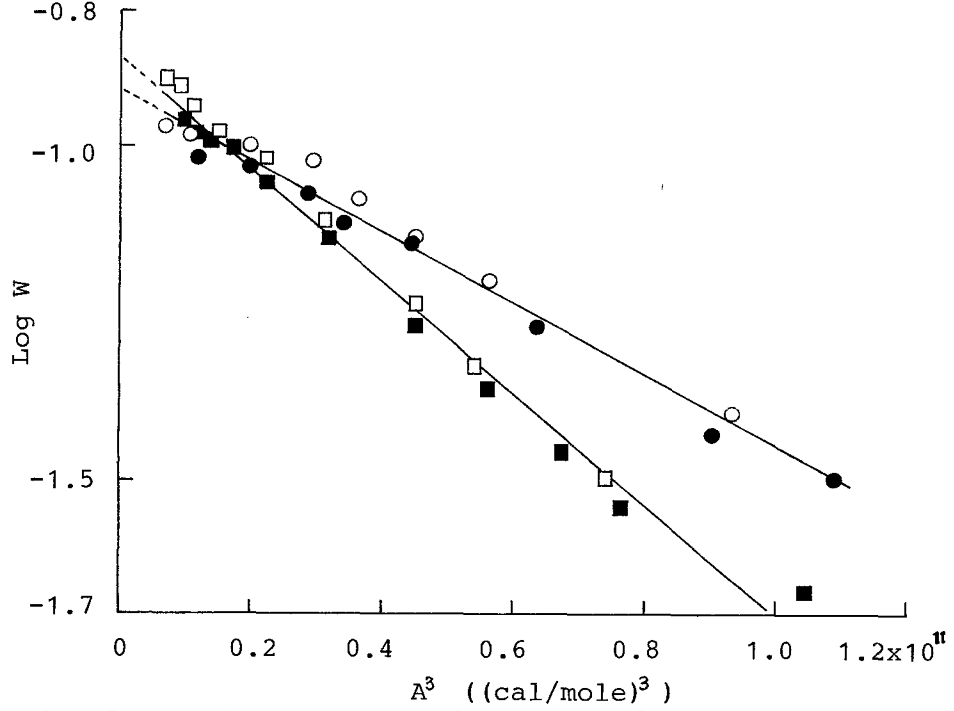

Fig. 2. Application of Dubinin-Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on MSC-5A and MSZ-5A. W: the filled volume of the adsorption space (mL/g); A: the decrease of free energy of adsorption; □: MSC-5A at 20 C; ■: MSC-5A at 30 C; ○: MSZ-5A at 20 C; ●: MSZ-5A at 30 C.

between Log W and A^3. Therefore, it appears that the adsorption of hydrogen sulfide on MSC-5A and MSZ-5A resulted in the volume filling of micropores with radii of less than 15 Å (ASTAKHOV et al. 1969).

Table 2 shows the results evaluated from the slopes of straight lines in Fig. 2. The relationship between E and ΔH_0 (heat of condensation of hydrogen sulfide, 4.46 kcal/mole; REID & SHERWOOD 1966) has been reported to be $E \div \Delta H_0$ at n = 3 (KAWAZOE et al. 1970). The results presented here agreed approximately with that reported by KAWAZOE et al. (1970). The fact that E of MSC-5A was somewhat smaller than ΔH_0 can be interpreted on the basis of dependence of the relation between E and ΔH_0 upon degrees of freedom of adsorbed molecules described by BARRER & LANGLEY (1958), that is, it can be explained that MSC-5A has partially the pores with radius larger than 5Å.

Table 2. Limiting Volume of Adsorption Space, Characteristic Energy of Adsorption, and n Value of the Dubinin-Astakhov Equation

Adsorbent	W_0 (mL/g)	E (cal/mole)	n
MSC-5A	0.1366	3726	3
MSZ-5A	0.1211	4339	3

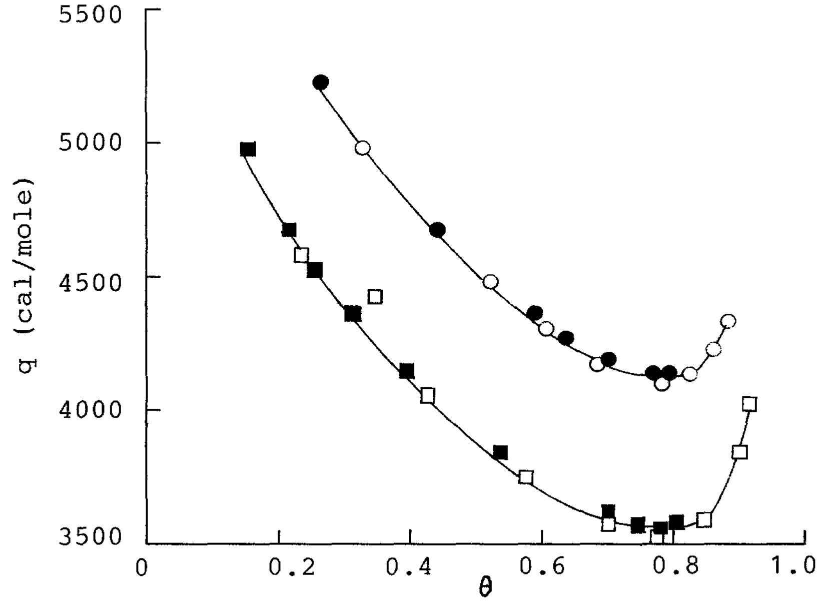

Fig. 3. Dependence of Net Differential Heat of Adsorption of Hydrogen Sulfide on MSC-5A and MSZ-5A upon the Degree of Filling of Micropores. q: net differential heat of adsorption; θ: degree of filling of micropores; □ : MSC-5A at 20 C; ■: MSC-5A at 30 C; ○: MSZ-5A at 20 C; ● : MSZ-5A at 30 C.

According to DUBININ (1972), 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,

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

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

where a_0 is the limiting amount adsorbed (mmole/g), a is the amount adsorbed, and α is the coefficient of thermal expansion of the adsorbate. Figure 3 shows the dependence of q of hydrogen sulfide on MSC-5A and MSZ-5A upon the degree of filling of micropores θ ($=a/a_0$). It will be noted that net differential heats of adsorption decrease with increasing θ but then pass through minima at about $\theta = 0.8$ and rise again in more increasing θ. As a_0 is the limiting adsorption value obtained when the whole adsorption space of micropores is filled by the adsorbed molecules (DUBININ 1972), a possible explanation for rising of q at above $\theta = 0.8$ is the change in adsorptive configuration of hydrogen sulfide adsorbed on the boundary between micropores and transitional pores (BEEBE et al. 1953).

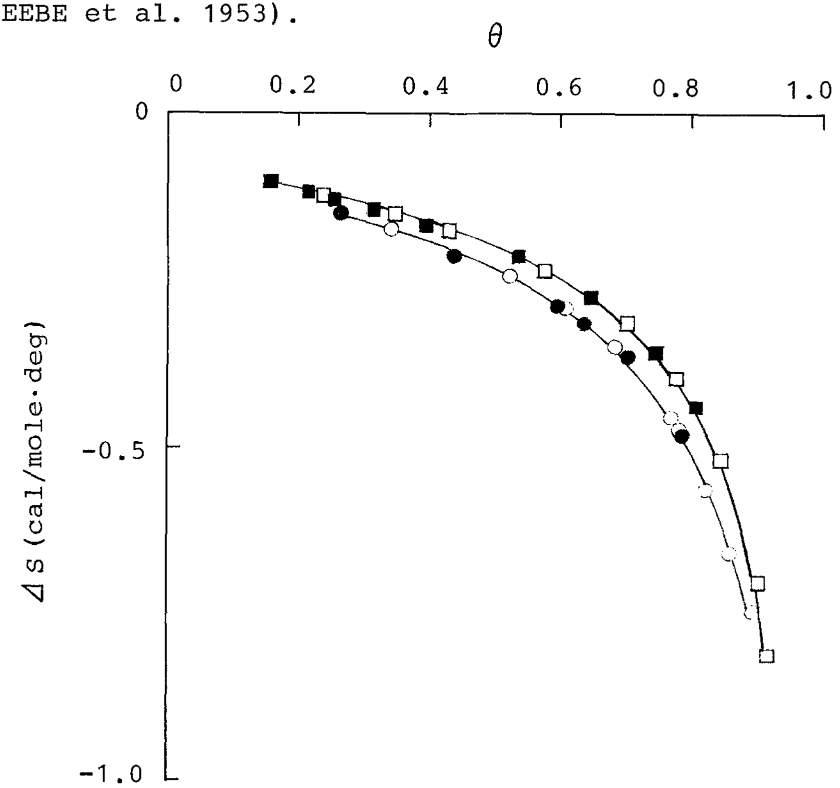

Fig. 4. Dependence of Differential Molar Entropy of Adsorption of Hydrogen Sulfide on MSC-5A and MSZ-5A upon the Degree of Filling of Micropores. ΔS: differential molar entropy of adsorption; θ: degree of filling of micropores; □: MSC-5A at 20 C; ■: MSC-5A at 30 C; ○: MSZ-5A at 20 C; ●: MSZ-5A at 30 C.

The continuous decrease of q with increase in θ indicates the energy heterogeneity of the volume of the adsorption space of micropores. The fact that the value of q of MSZ-5A was larger than that of MSC-5A is consistent with the result (DUBININ 1960) that the smaller the pore radius, the larger was the differential heat of adsorption.

Figure 4 shows the dependence of ΔS of hydrogen sulfide on MSC-5A and MSZ-5A upon θ. ΔS became smaller with increase in θ. This entropy change suggests that the hydrogen sulfide molecule is compactly filled in the micropores with increasing θ, that is, the molecule is possibly immobilized in the micropores with increasing adsorption. The fact that ΔS of MSZ-5A is smaller than that of MSC-5A suggests that hydrogen sulfide adsorbed on MSZ-5A is kept more compactly than that on MSC-5A.

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