Adsorption of Hydrogen Sulfide, Dimethyl Sulfide, and Their Binary Mixtures into Pores of N-Containing Activated Carbon

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The adsorption behavior of gas mixtures composed of hydrogen sulfide and dimethyl sulfide in the pores of N-containing activated carbon (N-CAC) was investigated on the basis of adsorption isotherms of the pure components and binary gas mixtures. Hydrogen sulfide and dimethyl sulfide were mainly adsorbed into smaller micropores and into larger micropores, respectively. The adsorption capacity of N-CAC for hydrogen sulfide was increased by 25-35% as compared with that of raw activated carbon (R-AC). The adsorption capacity of N-CAC for dimethyl sulfide was decreased by 20% as compared with that of R-AC. The experimental adsorption isotherms of binary gas mixtures at different molar ratios agreed closely with the theoretical adsorption isotherms on N-CAC. However, the experimental adsorption isotherms of the binary gas mixtures did not agree with the theoretical adsorption isotherms on R-AC and the amounts adsorbed on R-AC were very much smaller than the theoretical ones. These results indicated that adsorption of each component on N-CAC did not interfere with that of the other component, and that hydrogen sulfide and dimethyl sulfide entered micropores of different sizes in N-CAC. It was concluded that N-CAC is a characteristic adsorbent having a greater adsorption capacity for hydrogen sulfide in these binary gas mixtures. It seemed that adsorption of the binary gas mixtures was mainly competitive on R-AC and selective on N-CAC.

Keywords—binary gas mixture; hydrogen sulfide; dimethyl sulfide; N-containing activated carbon; selective adsorption; experimental adsorption isotherm; theoretical adsorption isotherm

Malodorous gas mixtures are often discharged into the atmosphere as wastes from industrial facilities such as sewage disposal plants, fish and animal processing plants, etc., and the concentration and composition ratio of these substances, which may also be toxic even at relatively low concentration, usually fluctuate greatly with time. Thus, it is important to find selective adsorbents which can remove the undesirable components specifically. However, only a few reports are available on adsorption of binary malodorous gas mixtures.1) Lewis et al.2) and Danner and Choi3) have reported on the adsorption of mixed hydrocarbon gases on activated carbon and zeolite. They found that data on the adsorption isotherms of the pure components are very helpful to clarify the occurrence of competitive or preferential adsorption of a binary gas mixture.2,3)

This report describes the adsorption behavior of hydrogen sulfide and dimethyl sulfide gas mixtures at different molar ratios in the pores of N-containing activated carbon (N-CAC)4,5) having a greater adsorption ability for hydrogen sulfide.

Experimental

Materials—Hydrogen sulfide gas was of certified grade from Seitetsu Kagaku Co., and its purity was indicated to be 99.9%. Dimethyl sulfide gas with a purity of better than 98.0%, was obtained from Seitetsu Kagaku Co. Activated carbon No. 1 (raw activated carbon (R-AC)) was obtained commercially from Wako Pure Chemical Inds. Ltd. (SDE 6318). Activated carbon No. 2 (N-CAC) was prepared by impregnating activated carbon No. 1 with 20% methylol melamine urea alcohol solution. The particle size of these adsorbents was 32-48 mesh. The procedure for
measurement of pore volume was described previously.\textsuperscript{7})

**Procedure for Pure Component Adsorption**—Adsorption isotherms of hydrogen sulfide and dimethyl sulfide on activated carbon were determined in an all-glass vacuum system similar to that described previously.\textsuperscript{8})

**Procedure for Binary Mixture Adsorption**—Adsorption isotherms of hydrogen sulfide and dimethyl sulfide gas mixtures (1:3, 1:1, and 3:1) were measured at 30°C and at equilibrium pressures up to approximately 100 Torr.

**Results and Discussion**

**Adsorption of Pure Hydrogen Sulfide and Dimethyl Sulfide**

Figure 1 shows the adsorption isotherms of pure hydrogen sulfide and dimethyl sulfide on R-AC and N-CAC at 30°C. The amount of hydrogen sulfide adsorbed on N-CAC was increased by 25—35% as compared with R-AC in the range up to 50 Torr and by 10—20% as compared with R-AC in the range up to 175 Torr. On the other hand, the amount of dimethyl sulfide adsorbed on N-CAC was decreased by approximately 20% as compared with R-AC in the range up to 175 Torr. Dubinin\textsuperscript{9}) pointed out that the pore structure of an adsorbent can be divided into three classes i.e., micropores (radius < 15—16 Å), transitional pores (15—16 < radius < 1000—2000 Å), and macropores (radius > 1000—2000 Å). Later, Dubinin\textsuperscript{10}) further classified the finest pores of adsorbent with equivalent radii up to 15—16 Å into

![Fig. 1. Adsorption Isotherms of Hydrogen Sulfide and Dimethyl Sulfide on R-AC and N-CAC](image1)

- R-AC; ○△, N-CAC.

![Fig. 2. Differential Pore Size Distribution Curves of R-AC and N-CAC](image2)

- R-AC; ○, N-CAC.

![Fig. 3. Experimental and Theoretical Adsorption Isotherms of Hydrogen Sulfide–Dimethyl Sulfide Gas Mixture (1:1) on R-AC and N-CAC](image3)

- —— experimental data; —— theoretical data; ●△, R-AC; ○△, N-CAC.
micropores (radius $< 6-7 \, \text{Å}$) and supermicropores ($6-7 < \text{radius} < 15-16 \, \text{Å}$). Figure 2 shows the differential pore size distribution curves of R-AC and N-CAC in the range up to 15 Å. The differential pore volume of N-CAC having pore radii smaller than 6.5 Å was 20% greater than that of R-AC. On the other hand, the differential pore volume of N-CAC with pore radii of 7.0–8.5 Å was much less than that of R-AC. The relationship between the amount adsorbed and differential pore size distribution can best be explained by assuming that hydrogen sulfide and dimethyl sulfide were mainly adsorbed into micropores (radius $< 6-7 \, \text{Å}$) and into supermicropores ($6-7 < \text{radius} < 15-16 \, \text{Å}$), respectively, in the range of low pressures.

**Adsorption of Binary Mixtures of Hydrogen Sulfide and Dimethyl Sulfide**

Figure 3 shows experimental and theoretical adsorption isotherms of hydrogen sulfide and dimethyl sulfide gas mixture (1:1) on R-AC and N-CAC at 30 °C. Theoretical adsorption isotherms of the binary mixture were calculated from the experimental adsorption isotherms of the pure components by using the law of partial pressures. The experimental adsorption isotherm of the binary gas mixture (1:1) on N-CAC agreed closely with the theoretical adsorption isotherm in the range up to 100 Torr. However, there was poor agreement in the case of R-AC; the amounts adsorbed on R-AC were very much smaller than the theoretical ones. Nishida et al. reported that the amount of hydrogen sulfide and methanethiol gas mixture (1:1) adsorbed on activated carbon was much less than the theoretical amount. Nishida et al. pointed out that hydrogen sulfide and methanethiol were competitively adsorbed on activated carbon. Lewis et al. and Danner and Choi reported that in the adsorption of a binary mixture of hydrocarbons on activated carbon and zeolite, each

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**Fig. 4. Experimental and Theoretical Adsorption Isotherms of Hydrogen Sulfide–Dimethyl Sulfide Gas Mixture (1:3) on R-AC and N-CAC**

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**Fig. 5. Experimental and Theoretical Adsorption Isotherms of Hydrogen Sulfide–Dimethyl Sulfide Gas Mixture (3:1) on R-AC and N-CAC**
component interfered with the adsorption of the other. Our results on the adsorption behavior of a binary gas mixture (1:1) on N-CAC were different from theirs, but our results on R-AC agreed with theirs. Our results indicate that in the adsorption of a binary gas mixture of hydrogen sulfide and dimethyl sulfide on N-CAC, each component did not interfere with the adsorption of the other component, and that hydrogen sulfide and dimethyl sulfide selectively entered micropores of different size in N-CAC. Moreover, the characteristic sizes obtained by using the Dubinin-Radushkevich equation for hydrogen sulfide on R-AC and N-CAC were 4.32 and 3.66 Å, respectively. The characteristic sizes for dimethyl sulfide on R-AC and N-CAC were 4.79 and 5.16 Å, respectively. The characteristic size of micropores is an average radius which corresponds to the characteristic point of the adsorption isotherm. R-AC showed little difference between the characteristic sizes for hydrogen sulfide and dimethyl sulfide. However, N-CAC showed a considerable difference. This difference in the case of N-CAC can best be explained by assuming that hydrogen sulfide and dimethyl sulfide enter mainly smaller micropores and larger micropores, respectively, and that hydrogen sulfide and dimethyl sulfide did not mutually interfere in adsorption on N-CAC in the low-pressure range. It was concluded that N-CAC is an adsorbent having a new character, because the adsorption behavior of a binary gas mixture on N-CAC was clearly different from those reported by Nishida et al.,1) and Lewis et al.,2) and Danner and Choi.3) Figure 4 shows experimental and theoretical adsorption isotherms of hydrogen sulfide and dimethyl sulfide gas mixture (1:3) on R-AC and N-CAC at 30°C. The experimental adsorption isotherm on N-CAC approximately agreed with the theoretical adsorption isotherm in the range up to 60 Torr. However, the amounts adsorbed on R-AC were much smaller than the theoretical ones. These results indicated that each component in the binary gas mixture did not interfere with the adsorption of the other when dimethyl sulfide was predominant in the gas mixture. Figure 5 shows the experimental and theoretical adsorption isotherms of hydrogen sulfide and dimethyl sulfide gas mixture (3:1) on R-AC and N-CAC at 30°C. The experimental amounts of gas mixture adsorbed on N-CAC were decreased by 10–25%, as compared with the theoretical ones, and those on R-AC were decreased by 40–80%, as compared with the theoretical ones in the range up to 50 Torr. This result indicated that when hydrogen sulfide was predominant in the binary gas mixture, each component in the binary gas mixture did not interfere markedly with the adsorption of the other on N-CAC and selectively entered micropores of different size. These results (Figs. 3—5) indicate that N-CAC is a characteristic new adsorbent whose adsorption properties do not depend markedly on the
composition ratio of hydrogen sulfide and dimethyl sulfide gas mixtures.

Figures 6, 7, and 8 show adsorption isotherms of hydrogen sulfide and dimethyl sulfide gas mixtures (1:3, 1:1, and 3:1, respectively) on R-AC and N-CAC at 30 ºC. The adsorption capacity of N-CAC for the 1:3 mixture was larger than that of R-AC in the range up to 5 Torr. The adsorption capacity of N-CAC for the 1:1 mixture was also larger than that of R-AC in the range up to 35 Torr. The same was also true for the 3:1 mixture up to 150 Torr. The results indicate that each component of the gas mixture was adsorbed more competitively on R-AC with increase in the molar ratio of hydrogen sulfide in gas mixture. On N-CAC, however, each adsorbate did not interfere with the adsorption of the other component, and hydrogen sulfide and dimethyl sulfide entered micropores of different sizes. It was concluded that N-CAC is a characteristic adsorbent having greater adsorption capacity for hydrogen sulfide from gas mixtures composed of hydrogen sulfide and dimethyl sulfide at different molar ratios.

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References