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Properties of Various Adsorbents for Removal of Hydrogen Sulfide Gas

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The adsorption of hydrogen sulfide gas on the thirty kinds of adsorbents (ten kinds of silicates, ten kinds of active carbons, and ten kinds of zeolites) was measured gravimetrically using Brunauer, Emmett, Teller (BET) apparatus with spring balance at30° and 50 mmHg in order to find out the most suitable adsorbent for the hydrogen sulfide gas removal by a dry process.

Among the thirty adsorbents, No. 23 (synthetic zeolite F-9) showed the largest amount of adsorption (mg/g). The relations between the amount of H_2S adsorbed per unit surface area (mg/m^2) and surface properties, the porous structure were investigated through surface pH, acid strength, acidity, basicity, adsorption isotherms, and pore size distribution.

The adsorption of hydrogen sulfide gas (mg/m^2) on the adsorbents except the active carbons was mainly determined by the porous structure of the adsorbents.

It is well known that hydrogen sulfide gas is not only poisonous but also rancid, and is designated by the Prime Minister's Office Ordinance[2] as one of the air pollution gases. The removal of hydrogen sulfide gas seems necessary in view of our daily lives.

Until now, hydrogen sulfide gas had been removed by several wet processes, for example, tripotassium phosphate,[3] sodium alanine or potassium dimethyl glycine,[4] several kinds of amines,[5] soda ash,[6] sodium carbonate,[7] and sodium thioarsenate[8] had been used as the absorbing solutions.

The present study is designed to secure some fundamental information on the removal of hydrogen sulfide gas by a dry process. In order to find out the adsorbent of the largest amount of hydrogen sulfide gas adsorbed (mg/g), the equilibrium adsorption of hydrogen sulfide gas on the thirty kinds of adsorbents was measured by a gravimetric method using Brunauer, Emmett, Teller (BET) apparatus with spring balance at 30° and 50 mmHg. The amount of hydrogen sulfide gas adsorbed per unit surface area (mg/m^2) of each adsorbent was particularly obtained here in order to clear the mechanism of adsorption. Surface pH's, acid strength, acidity, basicity, adsorption isotherms, and pore size distributions of the adsorbents used were measured. The relations between the amount of hydrogen sulfide gas adsorbed per unit surface area and the surface pH, the acid strength, the acidity, the basicity, the adsorption isotherms, the pore size distribution were studied here.

Experimental

Materials——Adsorbents used are shown in Table I. Adsorbents No. 1—No. 8 were manufactured by the authors, and other adsorbents were commercial ones. Sizes of adsorbents were 200—400 meshes.

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1) Location: *Yamashiro-cho, Tokushima-shi.*
2) *Prime Ministers Office Ordinance*, **39**, Enforcemet regulations of preventive law of offensive odor, Article 1 (1972).
3) A.L. Kohl, *Petroleum Processing*, **6**, 26 (1951).
4) R.M. Reed and N.C. Updegraff, *Ind. Eng. Chem.*, **42**, 2269 (1950).
5) H.W. Wainwright, G.C. Egleson, C.M. Brock, J. Fisher, and A.E. Sands, *U.S. Bur. Mines, Rept. Invest.*, **1952**, 4891.
6) J.J. Saunders, *Gas World*, **135**, 200 (1952).
7) H. Hollings, *Gas World*, **135**, 589 (1952).
8) P.L. Magill, F.R. Holden, and C. Ackley, "Air Pollution Handbook," McGraw-Hill Book Company, New York, 1956, pp. 13—94.

Specific surface areas of them were measured with BET apparatus using argon gas at liquid nitrogen temperature. H_2S gas was certified reagent grade (Seitetu Kagaku Co.) and its purity indicated 99.9%.

Procedure of Adsorption——As pretreatment conditions adsorbents were dried at 110° for 1 hour under 1×10^{-4} mmHg. Equilibrium amount of H_2S adsorbed at various pressure was measured for 30 minutes. The adsorption isotherms were determined by a gravimetric method using BET apparatus with spring balance at 30° and at pressures up to 50 mmHg. Amount of H_2S adsorbed (mg/g) at 30° and 50 mmHg were obtained from adsorption isotherms.

Surface pH——Surface pH's of adsorbents (No. 1—No. 10, No. 21—No. 30) were obtained using Nishicator (Nishio Universal Indicator; Nishio Kogyo Co., Ltd.). The method for measuring the pH's of No. 11—No. 20 was given by Hagiwara and others.[9]

Acid Strength, Acidity, and Basicity——Acid strength and acidity of adsorbents No. 1—No. 10, No. 21—No. 30 were measured by the Benesi's butylamine titration method,[10] and basicity of adsorbents No. 11—No. 20 were measured by the method of Okazaki and Toyoda.[11]

Pore Size Distribution——The method for measuring the pore size distribution of adsorbents was given by Urano and others[12] using methanol as an adsorbate at 3.0°.

Results and Discussion

The specific surface areas of the adsorbents used for adsorption of H_2S are shown in Table I. The amounts of H_2S adsorbed per unit weight and per unit surface area of adsorbents

Table I. Adsorbents Used for Adsorption of Hydrogen Sulfide Gas and Their Specific Surface Areas

No.	Adsorbent	Specific surface area (m^2/g)
1	Magnesium silicate ($SiO_2/MgO=1.62$)	428.6
2	Magnesium silicate ($SiO_2/MgO=2.28$)	324.5
3	Calcium silicate ($SiO_2/CaO=2.26$)	33.2
4	Calcium silicate ($SiO_2/CaO=0.62$)	17.1
5	Silica gel	44.5
6	Silica gel	313.2
7	Aluminium silicate ($SiO_2/Al_2O_3=0.53$)	114.5
8	Aluminium silicate ($SiO_2/Al_2O_3=0.27$)	14.8
9	Natural aluminium silicate	37.7
10	Synthetic aluminium silicate	72.0
11	Active carbon for gas chromatography	949.0
12	Active carbon	1285.5
13	Charcoal bone	81.7
14	Active carbon	1209.0
15	Active carbon	944.0
16	Active carbon (Shirasagi)	204.0
17	Active carbon (Norit "A")	586.0
18	Active carbon	495.0
19	Active carbon	204.0
20	Active carbon	930.0
21	Synthetic zeolite A-3	3.0
22	Synthetic zeolite A-4	49.7
23	Synthetic zeolite F-9	525.6
24	Molecular sieve 3A	23.1
25	Molecular sieve 4A	9.4
26	Molecular sieve 5A	41.1
27	Molecular sieve 13X	352.6
28	Molecular sieve 5A for gas chromatography	85.0
29	Molecular sieve 13X for gas chromatography	115.0
30	Natural zeolite	27.2

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9) S. Hagiwara, K. Tsutsumi, and H. Takahashi, *Nippon Kagaku Kaishi*, **1973**, 1369.
10) H.A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).
11) S. Okazaki and S. Toyoda, *Kogyo Kagaku Zasshi*, **73**, 478 (1970).
12) K. Urano, H. Mizusawa, and R. Kiyoura, *Kogyo Kagaku Zasshi*, **73**, 1911 (1970).

are shown in Table II. The amount of H_2S adsorbed per unit surface area (mg/m^2) was obtained by deviding the amount of H_2S adsorbed per unit weight by each specific surface area.

Table II. Amount of H_2S Adsorbed per Unit Weight and per Unit Surface Area on Adsorbents

No.	Amount of H_2S adsorbed		No.	Amount of H_2S adsorbed	
	(mg/g)	(mg/m^2)		(mg/g)	(mg/m^2)
1	23.65	0.0553	16	24.10	0.1179
2	21.23	0.0654	17	35.48	0.6046
3	0.00	0.0000	18	38.75	0.7827
4	0.00	0.0000	19	20.14	0.9870
5	0.00	0.0000	20	26.86	0.0289
6	7.67	0.0245	21	18.49	6.1650
7	4.12	0.0359	22	66.40	1.3365
8	7.28	0.4923	23	102.35	0.1944
9	3.89	0.1032	24	18.09	0.7836
10	15.83	0.2197	25	24.27	2.5790
11	23.27	0.0245	26	76.40	1.8545
12	29.28	0.0229	27	91.10	0.2580
13	8.77	0.1073	28	91.54	1.0935
14	38.60	0.0319	29	51.35	0.4465
15	32.45	0.0344	30	48.75	1.7920

Adsorption of hydrogen sulfide gas was measured at 30° and 50 mmHg.

The adsorbents No. 1 and No. 2 among the silicate adsorbents No. 14 and No. 18 among the active carbon adsorbents No. 11—No. 20, and the adsorbents No. 23, No. 27, and No. 28 among the zeolite adsorbents No. 21—No. 30, respectively, showed the largest amount of adsorption. The amounts of H_2S adsorbed (mg/g) on the active carbon adsorbents No. 18 and No. 14 were about twice as much as those of the silicate adsorbents No. 1 and No. 2 with the largest amounts of adsorption among No. 1—No. 10. The amounts of H_2S adsorbed (mg/g) on the zeolite adsorbents No. 23, No. 27, and No. 28 were about five times as much as those of No. 1 and No. 2. In particular, among the thirty kinds of adsorbents, the zeolites No. 23, No. 27, and No. 28 showed higher adsorption of H_2S gas (mg/g) than others, and were considered to be most suitable for practical purposes.

Assuming that the surface properties and the porous structures of the adsorbents are identical to one another, then the amount of H_2S adsorbed per unit surface area of each adsorbent is considered to be equal. However, in the third column of Table II were apparently admitted the differences in each amount of H_2S adsorbed per unit surface area. Therefore, the data presented here clearly show that the surface properties and the porous structures of the adsorbents are different from one another. In this study, the relations between the amount of H_2S adsorbed (mg/m^2) and the surface properties, the porous structure of each adsorbent were discussed through surface pH, acid strength, acidity, basicity, adsorption isotherm, and pore size distribution of each adsorbent.

1. On the Relations between the Amount of H_2S Adsorbed (mg/m^2) and the Surface Properties

Table III shows the acid strength of the adsorbents, and Fig. 1 shows the surface pH *vs.* the amount of H_2S adsorbed. Fig. 2(A) and Fig. 2(C), respectively, show the amount of H_2S adsorbed *vs.* the acidity of adsorbents No. 1—No. 10, and that of No. 21—No. 30. Fig. 2(B) shows the amount of H_2S adsorbed *vs.* basicity of No. 11—No. 20.

As H_2S is an acidic gas, it is conceivable that the stronger the basicity of adsorbent is, the more the amount of H_2S adsorbed (mg/m^2) is. Generally, the larger the negative value of an acid strength is and the smaller the positive value of an acid strength of No. 1, No. 9 and

Table III. Acid Strength of Adsorbents

No.	pK_a
1	-3.0——-5.6
2	$+1.5$——-3.0
3	$+4.8$—$+3.3$
4	$+4.8$—$+3.3$
5	$+1.5$——-3.0
6	$+4.8$—$+3.3$
7	$+4.8$—$+3.3$
8	$+4.8$—$+3.3$
9	-3.0——-5.6
10	-3.0——-5.6
21	$+9.4$—$+6.8$
22	$+6.8$—$+4.8$
23	$+6.8$—$+4.8$
24	$+3.3$—$+1.5$
25	$+3.3$—$+1.5$
26	-3.0——-5.6
27	-3.0——-5.6
28	$+3.3$—$+1.5$
29	$+3.3$—$+1.5$
30	-5.6——-8.2

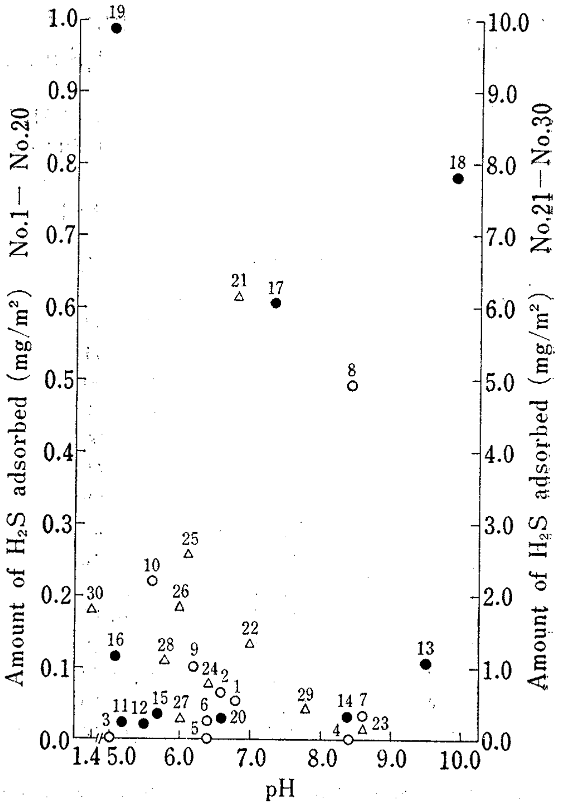

Fig. 1. Surface pH *vs.* Amount of H_2S Adsorbed

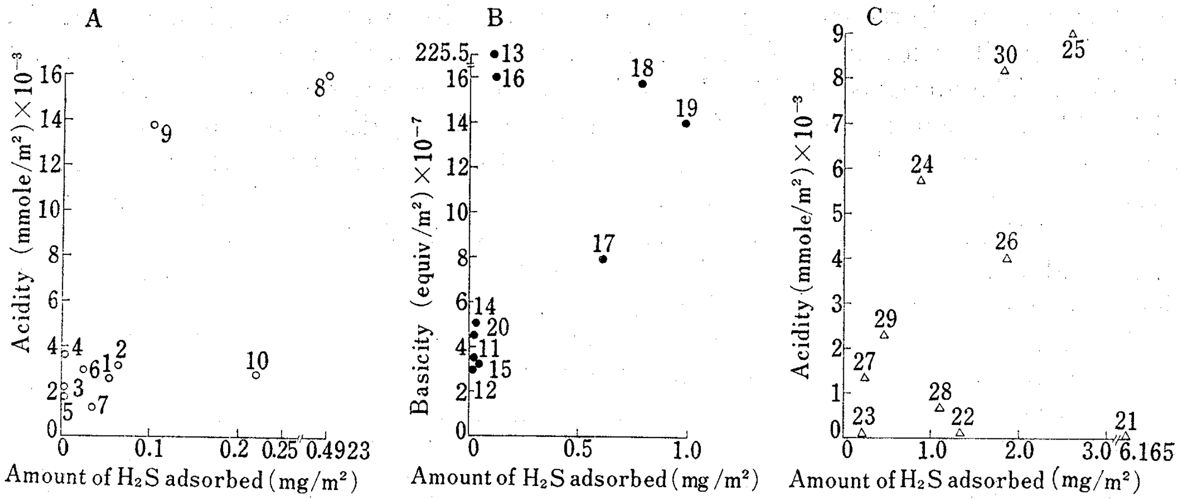

Fig. 2. Amount of H_2S Adsorbed *vs.* Acidity or Basicity

No. 10 were -3.0——-5.6, therefore, some acid sites of them were considered to be stronger than those of other adsorbents, but the amounts of H_2S adsorbed (mg/m^2) on them were more than those on others. The above results suggest that no relation between the acid strength of adsorbents and the amount of H_2S adsorbed (mg/m^2) was found among silicate adsorbents. Similarly, no acid strength of the zeolite adsorbents No. 21—No. 30 showed a linear relation with the amount of H_2S adsorbed (mg/m^2). The relation between the surface pH and the amount of H_2S adsorbed is shown in Fig. 1. Apparently no relation among these two items could be found. Assuming that the amount of H_2S adsorbed (mg/m^2) depends on the acidity (mmole/m^2), then it is conceivable that the less the acidity (mmole/m^2) is, the more the amount of H_2S adsorbed (mg/m^2) is, and similarly, that the more the basicity (equiv/m^2) is, the more the amount of H_2S adsorbed (mg/m^2) is. However, such the relation could not be admitted from the results of Fig. 2(A), Fig. 2(B), and Fig. 2(C). In view of the experimental facts that the amount of H_2S adsorbed (mg/m^2) was independent of the surface properties such an acid strength, surface pH, acidity, and basicity, it seems likely that the amount of H_2S adsorbed (mg/m^2) is caused by the porous structure of adsorbent.

2. On the Relations between the Amount of H_2S Adsorbed (mg/m^2) and the Porous Structure

Fig. 3, Fig. 4, and Fig. 5 show the adsorption isotherms of methanol on the silicates, the active carbons, and the zeolites, respectively. The amount of CH_3OH adsorbed (μl/g) at $P/P_0=1.0$ shows the pore volume of the adsorbent. Fig. 6, Fig. 7, and Fig. 8 show the pore size distribution curves obtained from the adsorption isotherms in Fig. 3, Fig. 4, and Fig. 5, respectively.

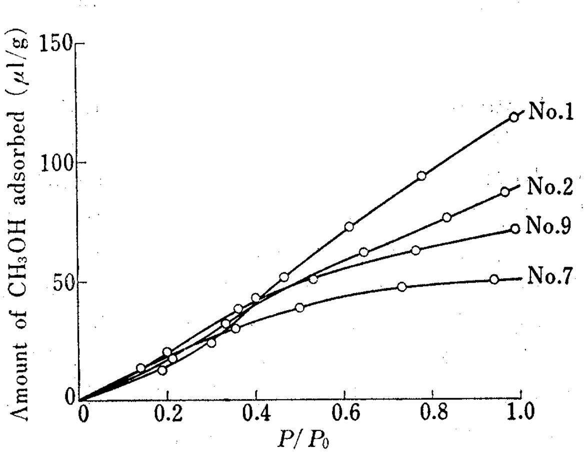

Fig. 3. Adsorption Isotherms of Methanol on Several Silicate Adsorbents

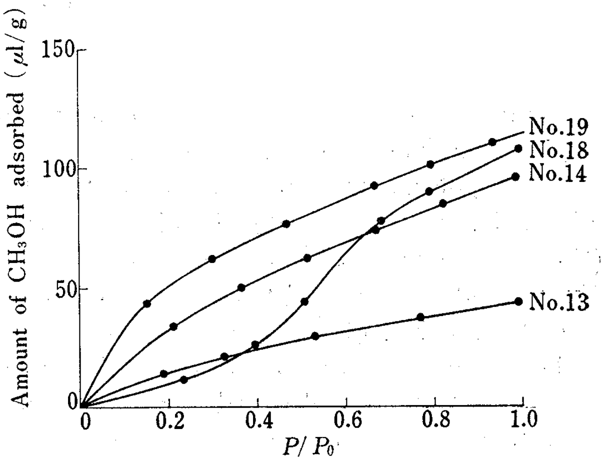

Fig. 4. Adsorption Isotherms of Methanol on Several Active Carbon Adsorbents

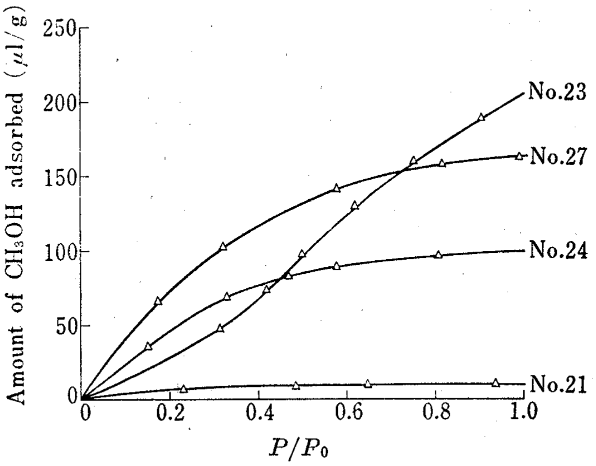

Fig. 5. Adsorption Isotherms of Methanol on Several Zeolite Adsorbents

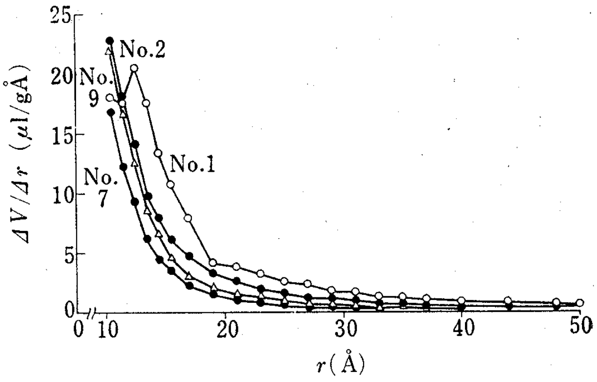

Fig. 6. Pore Size Distributions of Several Silicate Adsorbents

As Table II shows the amounts of H_2S adsorbed per unit weight (mg/g) of No. 1 and No. 2 were more than that of No. 9, whereas the amounts of H_2S adsorbed per unit surface area (mg/m^2) of these two adsorbents were less than that of No. 9. Such an inverse relation could be seen among the other adsorbents (see the Table II, *e.g.* No. 13 and No. 14; No. 23, No. 27 and No. 21, No. 24). The pore volume (the amount of CH_3OH adsorbed at $P/P_0=1.0$) of the adsorbents No. 1 and No. 2 showed larger than those of No. 9 and No. 7 (see Fig. 3) and as Fig. 6 shows, the differential pore volumes of No. 1 and No. 2 at radius greater than about 12Å were larger than those of others. It is possible to conclude from the results given above that the structures of No. 1 and No. 2 are more porous than those of No. 9 and No. 7. Therefore, it is con-

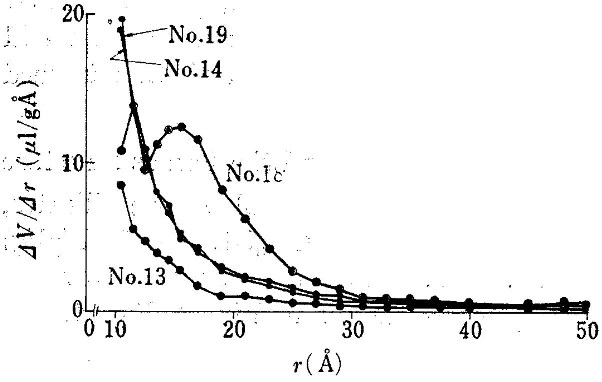

Fig. 7. Pore Size Distributions of Several Active Carbon Adsorbents

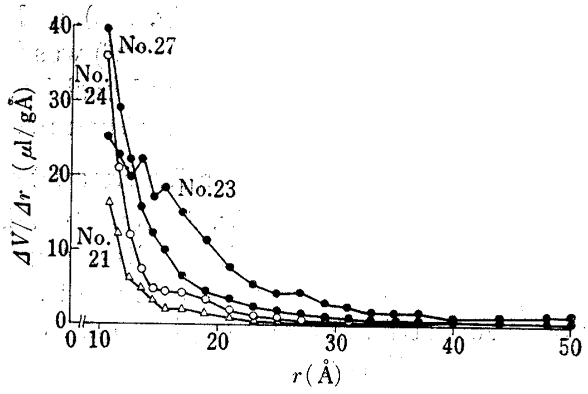

Fig. 8. Pore Size Distributions of Several Zerolite Adsorbents

ceivable that the amount of H_2S adsorbed per unit surface area (mg/m^2) of No. 1 and No. 2 are less than those of No. 2 than those of No. 9 and No. 7.

The porous structures of the active carbon adsorbents could be speculated through the adsorption isotherms in Fig. 4 and the pore size distribution curves in Fig. 7. The pore volume (the amount of CH_3OH adsorbed at $P/P_0=1.0$ in Fig. 4) of No. 19 was larger than those of No. 18 and No. 14, and the differential pore volume ($r>10$Å in Fig. 7) of No. 19 was larger than that of No. 14 and therefore, No. 19 was considered to be more porous than No. 14 and to be less amount of H_2S adsorbed (mg/m^2) than No. 14. However, as shown in Table II the amount of H_2S adsorbed (mg/m^2) on No. 19 was less than those on No. 18 and No. 14. It is therefore not unreasonable that the amounts of H_2S adsorbed (mg/m^2) on the active carbon adsorbents don't always depend on the porous structure of the adsorbents. The adsorption mechanism of H_2S on the active carbons remains obscure.

The porous structures concerning the zeolite adsorbents were speculated through Fig. 5 and Fig. 8. The results presented here (in Fig. 5 and Fig. 8) were in harmony with the results of the silicate adsorbents. This seems to indicate that the adsorbents No. 23 and No. 27 with less amounts of H_2S adsorbed (mg/m^2) than those of No. 24 and No. 21 are more porous than No. 23 and No. 27. The molecular size of argon gas was 14.4Å^2[13] and that of H_2S gas was 16.5Å^2[14] and therefore, it is supposed that the radius of argon gas are smaller than that of H_2S gas. The pore size distribution of pores of radius smaller than 10Å could not be obtained. However, the possibility also was considered that No. 1, No. 2, No. 23, and No. 27 *etc.* had so many pores in which argon gas could enter, but H_2S gas couldn't that the surface areas of these adsorbents were larger than those of others and the amounts of H_2S adsorbed per unit surface area of these four adsorbents was less than those of others.

As H_2S is very unstable, it easily changes into free S.[15] We had no apparatus to be characterized by its infrared spectrum, however, studies made by Deo, *et al.*[16] offered experimental evidence in support of this conclusion. Adsorption of H_2S on two different zeolites had been studied by infrared spectroscopy of the zeolite surfaces. Similar studies on active carbons had been made by Rozwadowski, *et al.*[17] and Olin, *et al.*[18] Rozwadowski, *et al.*[17] had pointed out that nearly the whole amount of H_2S irreversibly sorbed on carbons was free S, and Olin, *et al.*[18] supported the view that H_2S adsorbed on active carbon was oxidized into S by the active carbon as catalyst. Therefore, we suggest that H_2S adsorbed on adsorbents

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13) T. Keii, "Kyuchaku," Kyoritu Press, Tokyo, 1965, p. 97.
14) K. Boki, *Shikoku Acta Medica*, 30, 86 (1974).
15) S. Okuda, "Funtaikogyo to Kogaikosyukai Tekisuto," Hokuto Press, Kyoto, 1970, p. 78.
16) A.V. Deo, I.G. D. Lana, and W. H. Henry, *J. Catal.*, 21, 270 (1971).
17) M. Rozwadowski and T. Siedlewski, *Koks, Smola, Gaz*, **15**, 332 (1970).
18) H.L. Olin, V. Scarth, and W.L. Starkweather, *Gas Age-Record.*, **70**, 561 (1932).

was partially changed into S on surfaces of adsorbents. Further experimentation is necessary to explain fully this oxidation of H_2S into S.

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