Studies on Adsorption Removal of Odorous Pollutants (Acetaldehyde and Methyl Mercaptan) Adsorption of acetaldehyde on porous adsorbents

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INTRODUCTION

Acetaldehyde has recently been added to the list of chemicals in the control law for offensive odor in Japan, and its concentration in the atmosphere is limited by the law to the range of 0.05 to 0.5 ppm¹⁾. Acetaldehyde is emitted into the atmosphere particularly from the factories producing acetic acid, vinyl acetate, and chloroprene. It is well known that acetaldehyde irritates the mucous membrane of the eyes, nasal cavity, and pharynx²⁾, and may be formed as a secondary pollutant by photochemical reactions in the atmosphere. Thus far, it has mainly been removed by a wet process¹⁾ and by catalytic decomposition with iodine³⁾.

In my preceding paper⁴⁾, I studied the adsorption removal of methyl mercaptan. The present report gives the data on the adsorption of acetaldehyde having the same monomethyl group as methyl mercaptan. Adsorption of acetaldehyde by 20 kinds of adsorbents (activated carbon, zeolite, and silicate) was examined by a static method to find some suitable adsorbents for the removal of acetaldehyde. The mechanism of adsorption of acetaldehyde on adsorbents is discussed on the basis of the application of Dubinin equation⁵⁾ to adsorption isotherm and the pore size distribution.

MATERIALS AND METHODS

Materials: Acetaldehyde, commercially purified material, was purified by vacuum distillation. Activated carbon, zeolite, and silica gel used were commercial products, and magnesium silicate was prepared in our laboratory. Activated carbon Nos. 1~13 were different kinds of adsorbents.

Measurements of amounts adsorbed and the rate of adsorption: The adsorbents were dried at 110°C for 1 hr at 1×10^{-2} Torr before using. The equilibrium amount of acetaldehyde adsorbed at 30°C and up to 60,000 ppm was estimated from the stretching of a spring balance which became constant after the adsorption took place. The rate of adsorption was gravimetrically measured at the initial concentration about 90,000 ppm and 30°C, and expressed in a fractional approach to equilibrium⁶⁾.

Measurement of pore size distribution: The pore size distribution of several adsorbents was obtained by the method of Dollimore and Heal⁷⁾, the calculation being performed on a FACOM 203-28S (Fujitsu Co. Ltd.) computer using the FORTRAN program⁸⁾.

RESULTS AND DISCUSSION

Amount of acetaldehyde adsorbed: Table 1 shows the amount of acetaldehyde adsorbed on 20 kinds of adsorbents at 30°C. The amount shown in Table 1 was obtained from the

Table 1 Amount of acetaldehyde adsorbed on adsorbents at 30°C

No.	Adsorbent	Amount of acetaldehyde adsorbed (mg/g)						A _{CH₃SH} * (ppm) 60,000
		Equilibrium concentration of acetaldehyde (ppm) 1,000 5,000 10,000 20,000 40,000 60,000						
1	Activated carbon (4~7 mesh)	20.4	62.2	92.3	130.0	163.0	187.7	206.5
2	Activated carbon (4~8 mesh)	29.6	93.5	139.0	175.3	208.0	233.2	159.1
3	Activated carbon (4~7 mesh)	3.5	11.6	15.9	22.2	29.3	34.0	32.6
4	Activated carbon (4~7 mesh)	8.4	29.2	36.1	44.3	57.5	65.1	48.9
5	Activated carbon (4~7 mesh)	9.4	44.8	80.3	121.5	175.0	213.9	162.3
6	Activated carbon (4~7 mesh)	18.3	54.3	76.0	104.2	133.6	149.4	115.1
7	Activated carbon (4~7 mesh)	18.2	34.8	60.7	95.3	140.3	168.5	133.8
8	Activated carbon (7~9 mesh)	41.2	109.4	146.0	188.0	248.8	288.9	189.5
9	Activated carbon (8~20 mesh)	12.0	48.3	74.4	105.0	141.4	174.0	140.2
10	Activated carbon (12~30 mesh)	18.0	58.5	79.8	109.4	144.8	169.0	122.6
11	Activated carbon (4~7 mesh)	93.8	128.0	220.0	261.7	306.8	328.2	267.0
12	Activated carbon (8~20 mesh)	12.2	52.0	75.3	100.5	128.2	149.0	108.9
13	Activated carbon (12~30 mesh)	12.0	51.8	77.1	104.2	141.5	170.5	142.3
14	Synthetic zeolite A-3 (4~8 mesh)	60.0	92.6	98.5	102.8	107.0	110.6	97.2
15	Synthetic zeolite F-9 (4~8 mesh)	75.2	125.2	133.1	136.7	138.0	138.8	104.5
16	Molecular sieve 5A (1~16 mesh)	86.2	108.5	112.4	114.6	116.9	118.2	88.6
17	Molecular sieve 13X (1~16 mesh)	110.0	139.0	143.7	147.3	150.5	153.0	90.0
18	Silicagel (8~20 mesh)	32.5	84.8	97.4	109.6	129.2	139.6	82.4
19	Magnesium silicate (100~200 mesh)	95.6	118.7	127.2	136.2	147.4	153.5	68.5
20	Magnesium silicate (100~200 mesh)	106.1	126.6	133.5	140.7	150.2	155.8	79.0

* A_{CH_3SH} shows the amount of CH_3SH adsorbed on adsorbents at a equilibrium concentration 60,000 ppm adsorption isotherm at 30°C and up to 60,000 ppm. The higher the equilibrium concentration, the larger was the amount adsorbed on each adsorbent. Activated carbon No. 11, zeolite Nos. 14~17, and magnesium silicate Nos. 19 and 20 showed a larger amount adsorbed at lower concentrations of 1,000 and 5,000 ppm, while activated carbon No. 11 showed the largest adsorption among the twenty at a higher concentration of 60,000 ppm. The activated carbon No. 11 was found to be the most suitable adsorbent for the removal of acetaldehyde and methyl mercaptan with concentrations up to 60,000 ppm.

Application of Dubinin equation to adsorption isotherm: In general, adsorbents contain pores of various sizes, and adsorption properties of an adsorbent are intimately associated with its porous structure, the

Fig. 1 Application of Dubinin equation to adsorption isotherms of acetaldehyde on activated carbon (■—■: Adsorption isotherm of methyl mercaptan)

smallest pores (micropores) playing the principal role in adsorption. Dubinin⁵⁾ proposed, for the theory of gas adsorption by microporous adsorbents, the following equations which represent the development of Polanyi's potential theory of adsorption.

$$A = RT \ln(P_s/P) \quad \dots\dots\dots (1)$$

$$W = W_0 [\exp(-\kappa_0 A^2)] \quad \dots\dots\dots (2)$$

where A is the decrease of free energy in adsorption, R the gas constant, T the absolute temperature, P_s the saturated vapor pressure, P the equilibrium pressure, W the filled volume of the adsorption space, W_0 the limiting volume of the adsorption space, and κ_0 is the constant. The theory of physical adsorption of a gas in micropores which he proposed is termed the theory of the volume filling of micropores. Fig. 1 shows the application of Dubinin equation to adsorption isotherms of acetaldehyde on several kinds of activated carbon. A plot of $\log W$ versus A^2 of each adsorbent gave a straight line. Dubinin equation can be applied to adsorption isotherms of acetaldehyde on activated carbon Nos. 5, 8 and 11, and it was therefore concluded that adsorption of acetaldehyde in micropores of activated carbon resulted in their volume filling.

Rate of adsorption: The rate of adsorption is one of the parameters required in choosing a suitable adsorbent for practical use and, therefore, the fractional approach to the equilibrium of acetaldehyde on adsorbent is shown in Table 2. The fractional approach to the equilibrium⁶⁾ is given by

$$E = q/q_\infty \quad \dots\dots\dots (3)$$

where E is the fractional approach to the equilibrium, q the amount adsorbed at various elapsed periods, and q_∞ is the equilibrium amount adsorbed. It is thought that the longer the period at $E=0.5$ and $E=0.9$, the faster will be the rates of adsorption. Adsorption to approach $E=0.5$ was completed within about 3 min, except Nos. 14 and 15 but adsorbents Nos. 3, 8, 11, 14, 15 and 18 took a long time to approach $E=0.9$ and, in particular, adsorbents Nos. 14 and 15 took about 35 min. The rate of adsorption on activated carbon No. 11 was relatively fast and therefore, this is suitable for practical purposes.

Pore size distribution and the relation between the amount adsorbed and the pore volume:

The pore size distributions in the range of radii 6.5 to 300 Å was obtained in this experiment and Fig. 2 shows them particularly in the range of 6.5 to 24.5 Å to clarify the microporous structures of adsorbents. The curves except No. 5 rose to the constant volume at the radius of about 11 Å, and their volume was approximately constant in the range of 11 to 24.5 Å.

In general, adsorbents contain a variety of pore sizes but the results of Fig. 2 indicated that the micropore volumes at radii of less than about 11 Å occupied most of the pore volume up to 24.5 Å. It has previously been found in this laboratory that the amount of gas adsorbed on adsorbents was mainly determined by its pore volume^{4,9)}. Table 3 shows the amount of acetaldehyde adsorbed and the pore volume of several adsorbents. If it is

Table 2 Fractional approach to equilibrium of acetaldehyde on adsorbents

No.*	Time (min)		No.*	Time (min)	
	$E=0.5$	$E=0.9$		$E=0.5$	$E=0.9$
1	1.0	3.4	11	1.9	12.0
2	1.7	5.9	12	0.9	3.0
3	2.5	13.1	13	1.1	3.9
4	1.6	4.3	14	7.5	34.4
5	0.8	2.8	15	5.3	30.0
6	1.6	5.1	16	1.6	7.2
7	1.2	4.1	17	1.4	4.1
8	2.0	14.2	18	3.2	16.9
9	1.2	4.4	19	1.0	3.5
10	1.1	3.8	20	1.7	5.9

* No. 1~No. 13: Activated carbon

No. 14~No. 17: Zeolite

No. 18~No. 20: Silicate

Fig. 2 Pore size distributions of several adsorbents

Table 3 Amount of acetaldehyde adsorbed and pore volume of several adsorbents

No.	Amount adsorbed at 60,000 ppm (mmol/g)	Pore volume (ml/g)	
		$r \leq 300 \text{ Å}$	$r \leq 10.5 \text{ Å}$
1	4.26	0.5570	0.3495
4	1.48	0.2230	0.1233
5	4.86	0.7898	0.3888
6	3.39	0.3468	0.2117
8	6.56	0.6500	0.4839
11	7.77	0.6580	0.5575
14	2.36	0.1685	0.1405
15	3.15	0.2236	0.1465
17	3.47	0.2497	0.1744

Fig. 3 Amount adsorbed versus pore volume
(□—□ : Acetaldehyde, ■—■ : Methyl mercaptan)

assumed that the amount adsorbed on adsorbents is determined by their pore volume at radii of less than 300 Å, then the pore volume of Nos. 8 and 11 is estimated to be greater than that of No. 5, but the present results shown in Table 3 was contrary to their pore volume. The relation between the amount adsorbed and the pore volume in the range of 6.5 to 10.5 Å is illustrated in Fig. 3. An approximately linear relationship existed between the two and, therefore, it was confirmed that the amount adsorbed on adsorbents was determined by their micropore volume in the range of 6.5 to 10.5 Å. Amoore¹⁰⁾ reported that the length and the width of acetaldehyde were 4.0 and 2.5 Å, respectively. Adsorption of acetaldehyde in the micropores of adsorbents can be explained on the basis of its molecular size. The results of well suited application of Dubinin equation to adsorption isotherm and Fig. 3 indicate that adsorption of acetaldehyde in micropores ($r < 10.5 \text{ Å}$) of adsorbents resulted in their volume filling.

SUMMARY

The amount of acetaldehyde adsorbed and the rate of adsorption on 20 kinds of adsorbents were examined at 30°C. Activated carbon No. 11 was the most suitable adsorbent for the removal of acetaldehyde because of its higher adsorption capacity and faster rate of adsorption. The fact that Dubinin equation can be applied to adsorption isotherm of acetaldehyde indicated that adsorption of acetaldehyde in micropore resulted in volume filling. It was considered that the amount of acetaldehyde adsorbed on adsorbents was determined by their pore volume at radii of less than 10.5 Å rather than by their pore volume in the range of radii of 6.5 to 300 Å.

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悪臭物質（アセトアルデヒド，メチルメルカプタン）
の吸着除去に関する研究
多孔性吸着剤に対するアセトアルデヒドの吸着

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近年，悪臭防止法に加えられたアセトアルデヒドの除去に適した吸着剤を見い出し，さらに吸着機構を明らかにするため，多孔性吸着剤20種（活性炭13種，ゼオライト4種，ケイ酸塩3種）に対するアセトアルデヒドの吸着量と吸着速度を静的方法により測定した。

吸着剤20種のうち，活性炭 No. 11 は平衡濃度 1,000~60,000 ppm の範囲内で吸着量が最も多く，吸着速度は比較的速いため，アセトアルデヒドの吸着除去剤に適している。若干の活性炭に対するアセトアルデヒドの吸着等温線はDubinin式によく適合することから，アセトアルデヒドの吸着は活性炭のミクロ孔内への volume filling によって行われるものと考えられる。窒素ガス吸着法によって，若干吸着剤の細孔半径 $300\text{\AA}$ 以下の細孔分布を求めたが，いずれの吸着剤も半径約 $15\text{\AA}$ 以下（ミクロ孔）の細孔が発達していた。さらに吸着量と細孔容積の関係について検討した結果，アセトアルデヒドの吸着量と細孔半径 $10.5\text{\AA}$ 以下の細孔容積との間に相関性が認められた。したがってアセトアルデヒドの吸着剤はミクロ孔，とくに半径 $10.5\text{\AA}$ 以下の細孔容積の大きいものが適していることがわかった。

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