Adsorption of Methyl mercaptan on Surface Modified Activated Carbon

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Abstract

The influence of surface modification of activated carbon on the adsorption of methyl mercaptan in N_2 was investigated. The modification of the activated carbon was carried out by treatment with HNO_3/H_2SO_4 solutions, heat-treatment in Ar, and adsorption of cetylamine. Acid-treatment increased the adsorption of methyl mercaptan compared with the original activated carbon, and the adsorbed amounts increased with ratio of H_2SO_4 in HNO_3/H_2SO_4 solutions. This result suggests that hydrogen bonding between acidic groups formed by acid-treatment and thiol groups of methyl mercaptan plays a role in adsorption of methyl mercaptan on activated carbon.

Keywords: Activated carbon; Surface modification; Methyl mercaptan adsorption

1. Introduction

Methyl mercaptan (CH_3SH) is a highly odorous and volatile compound emitted to the atmosphere and the presence of a very little amount of CH_3SH in air (minimum odor threshold: about 5ppm) makes us uncomfortable. The removal of CH_3SH in air is important for our comfortable life. To remove methyl mercaptan from air, activated carbons are widely applied as one of the effective adsorbents[1-3]. In these applications of activated carbons, methyl mercaptan is physically or chemically adsorbed on activated carbons. In general, the adsorption of organic compounds by activated carbons is largely influenced by pore characteristics such as pore size, its distribution, morphology and surface property. Because methyl mercaptan molecule is small in size, surface property in pore characteristics is supposed to play an important role in the adsorption of methyl mercaptan. On the other hand, it was reported that the oxidation of methyl mercaptan to dimethyl disulfide takes place at the surface of activated carbons having functional groups such as carboxyl group in dry/wet air[4-6]. In addition, there are a few reports on the adsorption/oxidation of methyl mercaptan on surface modified activated carbons[7-9]. However, there is few reports discussing the real adsorption of methyl mercaptan on activated carbons.

In reference to the surface modification of activated carbons, the introduction of carboxyl groups and amino groups, and the preparation of functional group-free activated carbons have been reported [10-17]. The introduction of carboxyl groups on the surface of activated carbons by HNO_3 or H_2O_2 treatments was investigated[10-13]. The introduction of amino groups was carried out by various methods, e.g., the reduction of nitro group formed by a HNO_3/H_2SO_4 mixture [14-16], and the treatment with gaseous ammonia[17]. O the other hand, most functional groups generally vanish with heat-treatment under Ar or N_2.

From these points of view, in this work, we investigated the influence of surface modification of activated carbon by acid-treatment, heat-treatment, and adsorption of an amine compound on the adsorption of methyl mercaptan in N_2.

2. Experimental

2.1 Chemicals

Vinylidene chloride-co-methyl acrylate copolymer [Poly(VDC/MA)] was purchased from Aldrich. Nitric acid (13.4 N HNO_3), sulfuric acid (H_2SO_4), and cetylamine were purchased from Kanto Chemical Co. and used without further purification. 210 ppm of Methyl mercaptan in N_2 was used as methyl mercaptan gas.

2.2 Preparation of activated carbons

Activated carbon was prepared by carbonization followed by activation of Poly(VDC/MA) [18]. Activation was conducted with steam. The acid-treatment of the activated carbon was carried out with HNO_3/H_2SO_4 solutions. 1g of activated carbon was stirred in 100 cm^3 of HNO_3/H_2SO_4 solution for 3 h at 80°C. The treated activated carbons were separated by filtration and washed with deionized water several times under sonication until the pH of water become above 5. Then the activated carbons were dried in air at 100°C for 12 h and under vacuum at 150°C for 1 h. The activated carbons treated with HNO_3, HNO_3/H_2SO_4(1/1 ratio), and HNO_3/H_2SO_4(1/3 ratio) are denoted AC-At(1), AC-At(2), and AC-At(3), respectively.

The modification of the activated carbon with amine compound was carried out by adsorption of cetylamine. Activated carbon was immersed in a cetylamine/ethanol solution and stirred for 30 min at room temperature. Then the activated carbons were separated by filtration and dried under vacuum at room temperature for 2 h. The activated carbons prepared from 4 x10^{-6} and 3.3 x10^{-5} mol m^{-3} cetylamine solutions are denoted AC-Am(1) and AC-Am(2), respectively.

The heat-treatment of activated carbon (AC-Ht) was conducted at 600°C for 2 h under Ar atmosphere.

2.3 Measurements

BET specific surface area was determined from N_2 adsorption/desorption isotherms, which were obtained by a Quantachrome NOVA 3200. The estimations of mesopore specific surface area and size distribution were carried out according to BJH method[19]. The amounts of acidic groups on the activated carbons were estimated by a titration method[13].

The adsorption of methyl mercaptan was carried out by batch method. 20mg of activated carbon was placed in 0.85 x 10^{-3} m^3 of cylindrical vessel made from polymethyl metacrylate. After reducing the pressure of vessel under 1 mmHg, methyl mercaptan in N_2 was introduced into the vessel to atmospheric pressure. The adsorbed amount of methyl mercaptan was determined from the change of concentration of methyl mercaptan as a function of time. The concentration of methyl mercaptan was determined by gas chromatography using a J-Science GC7000FPD.

3. Results and Discussions

In order to investigate the influence of surface properties of activated carbons, we prepared the four kinds of activated carbons, which are quite different in surface properties. 1) Original activated carbon (AC): This was prepared by carbonization of Poly(VDC/MA), followed by steam activation. 2) Acid-treated activated carbons (AC-At): AC was treated with HNO_3/H_2SO_4 mixtures. These activated carbons are thought to have many acidic groups on the surface. 3) Cetylamine-adsorbed activated carbons (AC-Am): Cetylamine was adsorbed on the surface of AC. This treatment introduces many amino groups on the surface. 4) Heat-treated activated carbon(AC-Ht): AC was heat-treated in Ar atmosphere. By this treatment, functional groups of AC are decreased.

Figures 1 and 2 show N_2 adsorption/desorption isotherms of original activated carbon(AC), acid-treated activated carbons (AC-At(1), AC-At(2), and AC-At(3)), cetylamine-adsorbed activated carbons (AC-Am(1) and AC-Am(2)), and heat-treated activated carbon(AC-Ht) at 77K. The type of these isotherms is type I according to the IUPAC classification. The major uptake of N_2 in the adsorption/desorption isotherms of the activated carbons obtained occurs at relatively low relative pressure (< 0.2) and reaches the plateau at high relative pressure. These results indicate that the activated carbons obtained by various treatments were microporous. In the case of acid-treated activated carbons, the amounts of N_2 adsorbed decreased with increasing concentration of H_2SO_4 in acid solutions. Because the treatment with cetylamine alcoholic solutions highly decreased the amount of N_2 adsorbed, cetylamine seems to adsorb in pores of the activated carbon.

The pore characteristics of activated carbons estimated based on N_2 adsorption/desorption isotherms are shown in Table 1. AC is highly microporous and has high BET surface area more than 2600 m^2/g. In the case of acid-treated activated carbons, BET surface area decreased with the ratio of H_2SO_4 in HNO_3/H_2SO_4 solutions. It is assumed that the carbon porous structure of activated carbon is destroyed by strong oxidative effect by HNO_3/H_2SO_4 solutions and micropores are not detected. On the other hand, the cetylamine treatment of the activated carbon largely decreased BET specific surface area due to adsorption of cetylamine.

The amounts of acidic groups on the activated carbons estimated by a titration method [13] are shown in Table 1. The treatment of carbon surface with HNO_3/H_2SO_4 solutions generates large amounts of acidic groups, and the amounts of acidic groups increased with increase of H_2SO_4 ratio in HNO_3/H_2SO_4 solutions. The acidic groups per unit surface area of AC-At(3) are about 4 times higher than that of untreated AC. It is supposed that the addition of H_2SO_4 strengthens the oxidation effect for activated carbon. On the other hand, the amounts of acidic groups of AC decreased with heat-treatment in Ar. Acidic groups on carbon surface of the activated carbon are supposed to decompose in inert gas at high temperature. The amounts of cetylamine adsorbed on activated carbon, which was estimated by elemental analysis, increased with cetylamine concentration in aqueous solutions as shown in Table 1.

Fig.3 shows the adsorption of methyl mercaptan on the activated carbons as a function of time. The amounts of methyl mercaptan adsorbed on original activated carbon (AC) and heat-treated activated carbon increased with time at the initial time and reached the plateau values. The adsorbed amounts of methyl mercaptan on heat-treated activated carbon is lower than that on AC. Methyl mercaptan adsorbs physically, e.g., by a dispersive force, on the surface of heat-treated activated carbon. On the other hand, the amounts of methyl mercaptan adsorbed on acid-treated activated carbons and cetylamine-adsorbed activated carbons increased with time. In the case of acid-treated activated carbons, the adsorption of methyl mercaptan increased with concentration of H_2SO_4 in HNO_3/H_2SO_4 solutions used for treatment. Since the amounts of acidic groups of activated carbons increase with concentration of H_2SO_4 in HNO_3/H_2SO_4 solutions, the amounts of methyl mercaptan adsorbed are supposed to be influenced by acidic groups. Regarding the effect of carboxyl group, Bagreev et al. reported the catalytic effect on the oxidation of methyl mercaptan to dimethyl disulfide by oxygen in air under dry and wet condition. However, in this work, the adsorption of methyl mercaptan was carried out in dry N_2. Therefore, other factors, e.g., hydrogen bonding between carboxyl groups and thiol groups of methyl mercaptan rather than oxidation of methyl mercaptan are supposed to play a role in increase in adsorption of methyl mercaptan.In addition, it was reported that the adsorption/oxidation of methyl mercaptan is increased by the introduction of nitrogen on the surface of activated carbon[8,9]. However, the amounts of methyl mercaptan adsorbed on cetylamine-adsorbed activated carbons(AC-Am-1 and AC-Am –2) are much lower than those of acid treated activated carbons(AC-At-1, AC-At -2, and AC-At -3). It is supposed that this is attributed to the lower surface areas of AC-Am-1 and AC-Am-2 than those of AC-At-1, AC-At -2, and AC-At -3.

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Table 1 Pore characteristics, amounts of carboxylic group, and amounts of cetylamine of activated carbons

Sample	BET Surface area m^2/g	Mesopore Surface area m^2/g	Pore volume ml/g	Acidic group mmol/g	Amine group mmol/g
AC	2600	200	1.17	0.23	-
AC-At(1)	2190	204	1.02	0.50	-
AC-At(2)	2020	199	0.95	0.85	-
AC-At(3)	1370	184	0.68	1.20	-
AC-Am(1)	1360	130	0.63	-	0.64
AC-Am-(2)	718	58	0.34	-	1.20
AC-Ht	2460	199	1.13	0.10	-

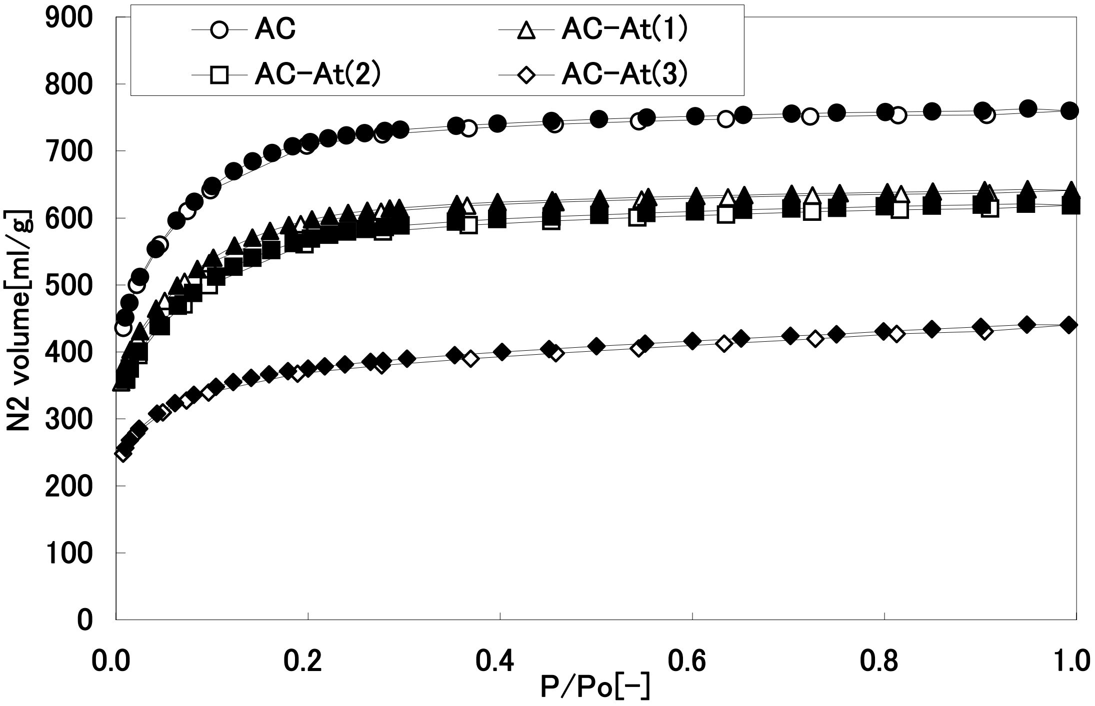

Fig.1 N_2 adsorption/desorption isotherms of acid-treated activated carbons. open:adsorption, closed:desorption

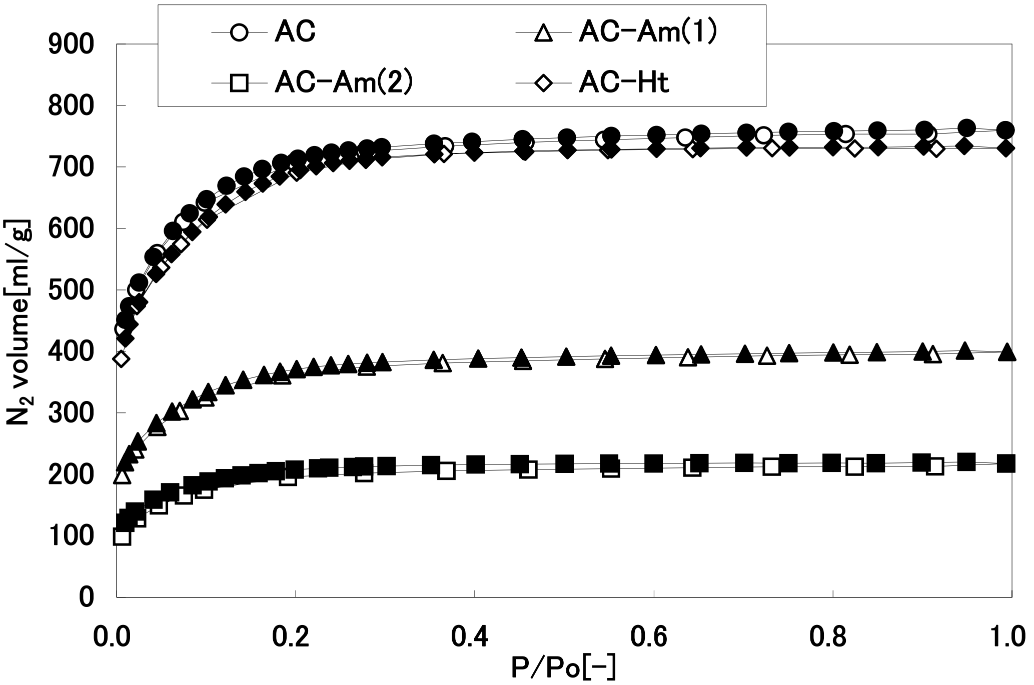

Fig.2 N_2 **adsorption/desorption isotherms of cetylamine-adsorbed and heat-treated activated carbons.** open:adsorption, closed:desorption

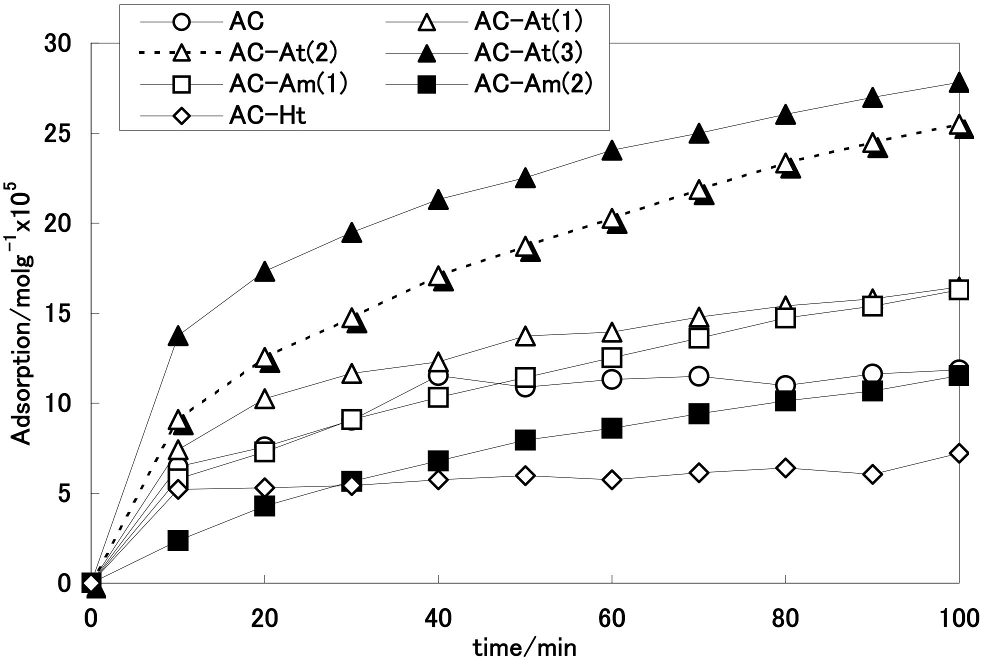

Fig.3 Adsorption of methyl mercaptan on activated carbons