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Role of copper chloride on the surface of activated carbon in adsorption of methyl mercaptan

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Abstract

In this paper, adsorption characteristics of methyl mercaptan on virgin activated carbon and copper chloride impregnated activated carbons were studied by using a dynamic adsorption method in a fixed bed. The activated carbons were characterized by nitrogen adsorption, XRD, TGA and solubility tests. The impregnation of copper chloride on the activated carbon significantly enhanced the adsorption capacity of methyl mercaptan, despite a notable decrease in microporosity. It is likely that copper chloride may act as adsorption site for methyl mercaptan. Copper chloride on the activated carbon in a range of 3–20 wt% Cu content was present mostly in the amorphous form of $CuCl_2$, according to the results of the solubility, XRD and TGA tests. Starting at 10 wt% in Cu loading, the adsorption capacity for methyl mercaptan decreases gradually. It is likely that a decrease in the degree of copper chloride dispersion and an accessibility of small pores may lead to the decrease in the adsorption capacity of the activated carbon for methyl mercaptan.

Keywords: Methyl mercaptan; Copper chloride; Activated carbon; Pore structure; Adsorption

1. Introduction

Methyl mercaptan (metanethiol, CH_3SH) is a volatile organic compound containing sulphur. It is a colorless gas with a smell like that of rotten or cooked cabbage. Methyl mercaptan is known to be produced in aerobic or anaerobic environments, mainly from natural sources, petroleum-refining processes, the wood-pulping industry, sewage treatment, and energy-related activities. Methyl mercaptan has a very low olfactory threshold of approximately 0.002 ppm, but at high concentrations methyl mercaptan is significantly toxic [1,2].

To remove the odor of methyl mercaptan from air, activated carbon is usually applied because of its porosity, large internal surface area and surface chemistry. Methyl mercaptan can be adsorbed on the activated carbon by physical or chemical adsorption. In the adsorption of methyl mercaptan, the pore structure and the surface chemistry of the activated carbon are very important.

The modification of the carbon surface has received considerable attention as a method to enhance the adsorption capacity of volatile organic compounds on activated carbon. The functional groups of the carbon surface can be modified either by the chemical and thermal treatments or by the impregnation method [3–5].

It has been reported that the adsorbed amount of methyl mercaptan increases with chemical treatments such as H_2O_2 and HNO_3 or with heat treatment at higher temperatures under nitrogen gas [6,7].

The objectives of this study are to determine the role of copper chloride on the surface of activated carbon in the adsorption of methyl mercaptan and to discover the effect of Cu loading on (1) the pore structure of the activated carbon and (2) the adsorption capacity of methyl mercaptan. Adsorption characteristics of methyl mercaptan on activated carbon were studied by using a dynamic adsorption method

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in a fixed bed. Virgin activated carbon and copper chloride impregnated activated carbons were characterized by nitrogen adsorption, XRD, TGA and solubility tests.

2. Experimental

2.1. Materials

Virgin activated carbon (coconut shell, 30/60 mesh) obtained from Kuraray (Japan) was used in the present investigations. Copper chloride impregnated activated carbons (having a Cu content of 3, 6, 10, and 20 wt%, respectively) were prepared by impregnation of the virgin activated carbon with an aqueous solution of $CuCl_2 \cdot 2H_2O$ (Aldrich) following the incipient wetness method. Before impregnating, the virgin activated carbon was dried for overnight at 110 °C. After impregnating, the samples were dried at 135 °C for overnight.

2.2. Methods

2.2.1. Dynamic adsorption test

Dynamic adsorption tests were carried out at 30 °C to evaluate the adsorption capacity of methyl mercaptan on all the samples. A sample of 0.1 g was placed in the center of a glass column (length 200 mm, diameter 9.0 mm). The column was placed in an electric furnace with an automatic temperature controller. A K-type thermocouple was inserted in the sample. Before the adsorption experiment, the sample was purged at 100 °C for 1 h with nitrogen flow of 100 ml/min. Methyl mercaptan in N_2 (350 ppm) was used as an adsorbate without further purification and the adsorbate was passed through the column of sample at 70 ml/min. The adsorbate flow was controlled by a mass flow controller. The inlet and outlet concentrations of the adsorbate were measured by gas chromatography with an FID detector (HP6890). The adsorbed amount of methyl mercaptan was calculated directly from breakthrough curves [8,9].

2.2.2. Nitrogen adsorption

Nitrogen isotherms were measured using an AS1 instrument (Quantachrom) at −196 °C. Before the experiment, the samples were heated at 100 °C and then outgassed overnight at the same temperature under a vacuum of 10^{-6} Torr. The isotherms were used to calculate the BET specific surface areas (S), total pore volumes at $P/P_0 = 0.995$ (V_t) and micropore volumes (V_m). Micropore volumes were determined using t-plot method.

2.2.3. A solubility test

To perform a simple solubility test for copper chloride impregnated carbon, a 1 g sample was placed in a beaker containing 100 ml of distilled water. Distilled water easily dissolves $CuCl_2$ compared to the insoluble compounds such as basic chlorides and oxychlorides [10]. The beaker was sealed and shaken for 48 h at room temperature, and the mixture was run through a membrane filter. Fifty milliliters of the solution was placed in a beaker containing 50 ml of 0.1 N NaOH solution. The bluish copper precipitate such as $Cu(OH)_2$ appeared immediately. It seemed to be due to a reaction of NaOH and copper chloride compounds [11].

The beaker was sealed and shaken for 48 h to reach equilibrium, and then the mixture was run through a membrane filter. The consumed amount of NaOH during the reaction was obtained from the titration of NaOH and HCl [12]. The concentration of Cu on the surface of the sample was determined from the consumed amount of NaOH, assuming the following reaction, in which NaOH reacted with $CuCl_2$

$$2NaOH + CuCl_2 \rightarrow Cu(OH)_2 + 2HCl. \quad (1)$$

2.2.4. XRD and TGA

XRD patterns of the samples were obtained by the Rigaku D/MAX2200 X-ray diffractometer with Cu$K\alpha$ radiation. The XRD experiments were conducted at 20 kV and 30 mA. Diffraction intensity was measured between 20° and 70° (2θ) at the rate of 5°/min. The TGA experiments of the samples were carried out using TA Instruments thermal analyzer. The instrument was set to increase the temperature at a rate of 10 °C/min in nitrogen atmosphere with a flow rate of 100 ml/min.

3. Results and discussion

In the adsorption process of methyl mercaptan on activated carbon, the pore structure of the activated carbon has been reported to affect the adsorption capacity of methyl mercaptan [6,7]. Information about the pore structure of an adsorbent can be obtained through an adsorption isotherm.

To evaluate the pore structure through increasing Cu loading, nitrogen adsorption experiments on the samples were carried out. The structural parameters of the samples studied, micro volumes (V_m), total pore volumes (V_t) and BET surface areas (S), were calculated from the nitrogen adsorption isotherm and the results obtained were collected in Table 1. The ratio of the volume of the micropore volume to the total pore volume (V_m/V_t) is calculated. The ratio means the degree of microporosity.

Table 1
Parameters calculated from nitrogen adsorption isotherms

Sample	S (m^2/g)	V_t[a] (cc/g)	V_m[b] (cc/g)	V_m/V_t[c]
Virgin/AC	1230	0.719	0.651	0.91
3 wt% Cu/AC	923	0.545	0.488	0.90
6 wt% Cu/AC	843	0.494	0.435	0.88
10 wt% Cu/AC	756	0.468	0.411	0.88
20 wt% Cu/AC	624	0.368	0.318	0.86

[a] Total pore volume at $P/P_0 = 0.995$.
[b] Micropore volume calculated from t-plot method.
[c] Ratio of micropore volume to total pore volume.