ACTIVATED CARBONS AS ADSORBENTS OF METHYL MERCAPTAN

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Introduction

An objective of this paper is to describe in detail the adsorption of methyl mercaptan from wet air streams on activated carbons. However, the process has been studied [1-3], to our best knowledge there is no extensive study of this phenomenon. This is due to the low odor threshold for methyl mercaptan and its toxic properties. The purpose of the present work is to make an attempt to identify the reaction products and to study the influence of the carbon surface on the removal/oxidation of methyl mercaptan. The preliminary research clearly shows high (100%) efficiency of methyl mercaptan removal on activated carbons at ambient conditions. Our outgoing research focuses on throwing more light on the mechanism of adsorption/oxidation and on a specific role of various surface features.

Experimental

Materials. Four commercial activated carbons of various origins were used in this study. They are as follows: BAX-1500 (wood based -Westvaco), S208 (coconut shell - Waterlink Barnabey and Sutcliffe), Centaur (catalytic carbon - Calgon), and BPL (bituminous coal - Calgon).

The as received materials were studied as adsorbents for methyl mercaptan in the dynamic tests described below. After this test and purging with air the samples are considered as exhausted and they are designated with an additional letter "E".

Methods. Dynamic tests were carried out at room temperature to evaluate the capacity of the sorbents for CH_3SH removal under wet conditions. Adsorbent samples were ground (1-2 mm particle size) and packed into a glass column (length 370 mm, internal diameter 9 mm, bed volume 6 cm^3) and prehumidified with moist air (relative humidity 80 % at 25 ^oC) for one hour. The amount of water adsorbed was estimated from the increase in the sample weight. Moist air (relative humidity 80 % at 25 ^oC) containing 0.3 % (3,000 ppm) CH_3SH was then passed through the column of adsorbent at 0.5 L/min. The breakthrough of CH_3SH was monitored using a MicroMax monitoring system (Lumidor) with an electrochemical sensor. The test was stopped at the breakthrough concentration of 50 ppm. The adsorption capacities of each sorbent in terms of mg of CH_3SH per g of carbon were calculated by integration of the area above the breakthrough curves, and from the CH_3SH concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent. For each sample the CH_3SH test was repeated at least twice. The amount of weakly adsorbed CH_3SH was evaluated by purging the adsorbent column with carrier gas at 0.35 L/min immediately after the breakthrough experiment. The CH_3SH concentration was monitored until it dropped to 1 ppm. The process took about up to 3 hours depending on the type of adsorbent.

Nitrogen adsorption isotherms were measured using an ASAP 2010 analyzer (Micromeritics, Norcross, GA, USA) at -193 ^oC. Before the experiment the samples were degassed at 120 ^oC to constant pressure of 10^{-5} torr. The isotherms were used to calculate the specific surface area, S_{N2}; micropore volume, V_{mic} and total pore volume, V_t. All the parameters were determined using Density Functional Theory (DFT) [4].

To evaluate the surface pH a 0.4 g sample of dry adsorbent was added to 20 mL of deionized water and the suspension stirred overnight to reach equilibrium. The sample was filtered and the pH of solution was measured using an Accumet Basic pH meter.

Thermal analysis was carried out using TA Instruments Thermal Analyzer (New Castle, DE, USA). The heating rate was 10 deg/min in a nitrogen atmosphere at 100 mL/min flow rate.

Results and Discussion

The methyl mercaptan breakthrough curves are presented in Figure 1. The methyl mercaptan breakthrough capacities calculated from those experiments are summarized in Table 1 along with the pH values of the carbon surfaces, before and after exhaustion, and the amount of water adsorbed during the prehumidification step. The data collected indicate differences in the performance of carbons. The exceptionally high capacity was found for coconut shell-based carbon, S208. Although the large capacity was also found for Centaur, its performance is still worse than that for S208. There are also differences in the adsorption of methyl mercaptan on wood based and bituminous coal based carbon. For the former the capacity is basically nil and the breakthrough occurred just seconds after the tests started. For the latter material the capacity is similar to that obtained on catalytic carbon, Centaur.

Table 1. pH of the surface, amount of water preadsorbed, and CH_3SH breakthrough capacities for the materials studied.

Sample	pH/pHE	Amount of water	CH_3SH capacity [mg/g]	CH_3SH desorbed [mg/g]
BAX	7.03/7.00	165.5	0	0
BPL	7.96/6.90	86.1	251	0.04
S208	10.11/10.01	94.3	349	0.07
Centaur	7.30/5.24	93.4	230	0.08

As seen from Table 1, the capacity on Centaur is large, however its pH is close to neutral. On the other hand, the capacity of BAX is nil, in spite of the fact that its average pH is almost equal to that for Centaur. Moreover, the large capacity is reported for BPL carbon whose pH is only slightly higher than that for BAX. Discussing these data we have to take into consideration that the pH reported in Table 1 is the average pH of the carbon surface and the "local" pH inside pores can be different, especially when pores are small and functional groups are present at their entrances [5, 6]. Since in the case of CH_3SH dissociation must be important as for H_2S it is likely that some pH threshold exists and the pH of BAX can be bellow that value [7]. Another factor, which should be taken into account is the manufacturing technology. The neutral pH of the as received BAX is likely the result of surface neutralization with base after activation with phosphoric acid, which usually results in carbons with acidic pH [8].

Although the pH of carbons decreased after methyl mercaptan adsorption no relationship is found between the amount adsorbed and the variations in pH. The effect on catalytic carbon may suggest that acids are formed on the surface as a result of methyl mercaptan oxidation. Since a decrease in the pH is relatively small compared to hydrogen sulfide oxidation where sulfuric acid was formed [5, 6, 8, 9] it is possible that small amount of sulfur-containing acid along with disulfides, are the products of the surface reaction. For other carbons, even with the large amount adsorbed as in the case of S208, a decrease in pH is very small.

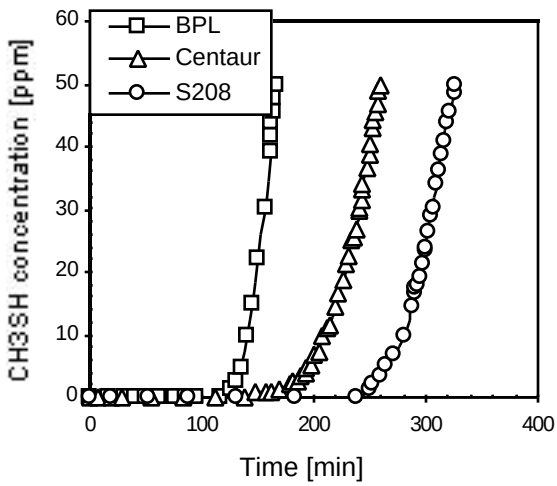

Figure 1. CH_3SH breakthrough curves.

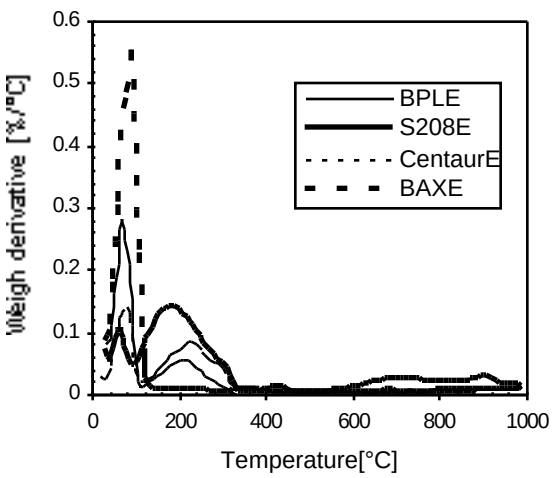

Figure 2. DTG curves in nitrogen for exhausted samples.

The species present on the carbon surface after adsorption can be analyzed using DTG curves obtained in nitrogen. This method was used for the analysis of the products of hydrogen sulfide oxidation [5, 6, 9], sulfur dioxide adsorption [10], and chemisorption of organosulfur compounds on gold [11]. It is assumed that the peak at temperature smaller than 100 ^oC represents the desorption of weakly adsorbed species (Figure 2) likely water. The peak between 100 and 300 ^oC might represent desorption of disulfides [11], or removal of methane sulfonic acid relatively weakly adsorbed on the surface. Since methyl mercaptan is expected to be adsorbed very weakly on the surface due to its physicochemical properties (e.a. CH_3SH is desorbed from the gold surface between -83^oC and -50 ^oC [11]), we exclude its presence in the adsorbed phase. For all carbons after exhaustion the two mentioned above peaks are present (Figure 2). The second peaks show the features of heterogeneity of species manifested by the presence of a shoulder around 300 ^oC with a sharp decrease in the weight loss. This is seen in the most pronounced way for S208 carbon. The shoulder may represent decomposition of surface oxygen complex, $CH_3SSCH_3 \cdot n\ O_2$, which desorbs as SO_2 or SO_3. Oxygen, if present in this form, does not contribute to a decrease in the pH value of the carbon surface after exhaustion. Supporting for this is its temperature of desorption which is close to the temperature of desorption of weakly adsorbed SO_2 or SO_3 on activated carbons [10]. In the case of Centaur, owing to its decrease in the pH after exhaustion, we may expect desorption of small amount of sulfur-containing acid as a ~300 ^oC shoulder [12]. This peak likely represents sulfur containing acids. This is the effect of nitrogen containing catalytic centers located in small pores as described in the case of hydrogen sulfide adsorption [6].

Another reason for the low capacity of BAX carbon, besides its low pH, may be in its pore structure [13]. BAX and BPL have the highest pore volume, whereas Centaur - the lowest. As expected, the same trend is found in the volumes of micropores and surface areas. The most homogeneous from the point of view of microporosity is S208, whereas BAX is the most heterogeneous sample. The small pores are also present in Centaur. The presence of large pores can affect the sorption capacity of BAX carbon. Even if its pH is favorable for the dissociation of methyl mercaptan in the pore system, which likely enables its oxidation, the pores can be too big to enhance the methyl mercaptan adsorption, especially when preadsorbed water is present (7.7 weight % as indicated from Table 1).

Conclusions

Based on the results presented above, some direct relationship between the surface features and the amount of methyl mercaptan adsorption can be found. Moreover, there is an indication of the competition for adsorption sites between water and dimethyl sulfide. This hypothesis seems to be reasonable if we take into account the lack of disulfide solubility in water. The formation of disulfides is enhanced by the presence of water, as a result of dissociation of methyl mercaptan. Disulfides, when formed, are expected to be stronger adsorbed on the surface of carbon than water. Taking into account their incompatibility with water molecules it is likely that they replace adsorbed water molecules.

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