

CATALYTIC PROPERTIES OF ACTIVATED CARBON SURFACE IN THE PROCESS OF ADSORPTION/OXIDATION OF METHYL MERCAPTAN

Svetlana Bashkova¹, Andrey Bagreev², Teresa J. Bandosz^{1,2}

¹ Department of Chemistry, The Graduate School of the City University of New York

² The City College of New York

Corresponding author e-mail address: tbandosz@ccny.cuny.edu

Introduction

This research focuses on activated carbons as adsorbents and catalysts for the removal of methyl mercaptan (MM) – odoriferous sulfur-containing compound commonly added to natural gas for leak detection purposes. Activated carbons are well known for their exceptional ability to adsorb some acidic gases. The application of activated carbons to remove hydrogen sulfide (one of the natural gas contaminants) is widely described in literature [1, 2].

The main objective of this paper is to link the efficiency of activated carbons as MM adsorbents to their surface and structural characteristics. Among the features of carbon responsible for MM immobilization at ambient conditions are pore size and pore volume [3-5], surface oxygen groups [4], surface pH [5], and the affinity of carbon to adsorb water [3, 5]. Moreover, different functional groups on the surface or/and metal ions such as iron can catalyze the oxidation of mercaptans to disulfides [6, 7].

Experimental

Materials

Adsorption of methyl mercaptan (MM) was performed on several samples of activated carbons of various origins. Among the carbons studied were BAX-1500 (wood based - Westvaco), S208 (coconut shell based carbon - Waterlink Barnabey and Sutcliffe), Centaur[®] (coal-based catalytic carbon - Calgon), BPL (bituminous coal - Calgon), and PCB (coconut shell-Calgon). The initial samples were washed in a Soxhlet apparatus to a constant pH of a leachate. PCB sample (25 ml) was impregnated with 0.05 M solution of FeCl₃ x 6H₂O (100 ml), stirred for 20 hours, filtrated and then heated at 200 °C for 3 hours and washed with water in a Soxhlet apparatus.

Methods

CH₃SH breakthrough capacity

Dynamic tests were carried out at room temperature to evaluate the capacity of the sorbents for CH₃SH removal under wet conditions. Adsorbent samples were ground,

packed into a glass column and prehumidified with moist air for one hour. The amount of water adsorbed was estimated from the increase in the sample weight. Moist air containing 0.3 % (3,000 ppm) CH₃SH was then passed through the column of adsorbent at 0.5 L/min. The breakthrough of CH₃SH was monitored using a Micromax monitoring system (Lumidor) with an electrochemical sensor calibrated with MM. The test was stopped at the breakthrough concentration of 50 ppm.

pH of carbon surface

0.4 g of carbon powder was placed in 20 mL of water and equilibrated during night. Then the pH of the suspension was measured. For exhausted samples an additional letter "E" is added (pHE).

Sorption of nitrogen

Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. The isotherms were used to calculate the specific surface areas (S), micropore volumes (V_{mic}), total pore volumes (V_t), average micropore sizes (L_{mic}), and pore size distributions (DFT) [8].

Thermal analysis

Thermal analysis was carried out using TA Instruments Thermal Analyzer. The instrument settings were: heating rate 10 °C/min in nitrogen atmosphere with 100 mL / min flow rate.

Ash content

Total ash content was evaluated as residue in air after heating to 1000 °C.

Boehm titration

Surface chemistry was evaluated using the Boehm titration method [9]. In this approach the numbers of acidic sites are calculated from the titration with NaOH and the number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

XRF

X-Ray Fluorescence analysis was applied to study the elements present in the carbon. For this purpose SPECTRO Model 300T Benchtop Multi-Channel Analyzer from ASOMA Instruments, Inc. was used. It contains a titanium (Ti) target x-ray tube with Mo-2mil filter and high resolution detector without a filter. The following acquisition conditions were used: voltage – 24 kV, current – 80µA, count time – 40 sec, and warm-up – 4 min. Instrument reference temperature was 20 °C; background conditions: lower ROI – 12.000, upper ROI – 17.000.

Results and Discussion

To investigate the ability of activated carbons to adsorb methyl mercaptan, breakthrough test was carried out at room temperature. The highest amount adsorbed

was found for the Centaur[®] carbon. The capacities of BPL and S208 carbons are also significant compared to BAX and PCB. To understand what is governing the process of MM adsorption on different carbon samples, we have to get a deeper insight on the nature of carbons under investigation and the features that lead to the differences in their capacities.

A chemical analysis of the carbon surface was done using Boehm titration. Figure 1 shows the dependence between the MM adsorption capacity and the density of basic groups. Good correlation is found for all the samples except PCB. Both BPL and S208 samples are very active towards the adsorption of MM even though they are less basic than PCB. This indicates the possible contribution of metal impurities to the adsorption process. To specify the metals present in the carbon, XRF method was applied. The results showed that BPL carbon is rich in iron and its amount is much higher ($\approx 0.4\%$) than that for the rest of the samples, which could be a reason for its high MM removal capacity. Iron oxide is commonly used as an activated carbon impregnate to increase the removal of hydrogen sulfide and mercaptans. On the other hand, an unexpected behavior of PCB carbon can be related to the lack of iron and other catalytically active metals on its surface (Figure 1). Another coconut-shell based carbon - S208 with similar surface characteristics also has small iron content but its high capacity may be related to the presence of significant amount of.

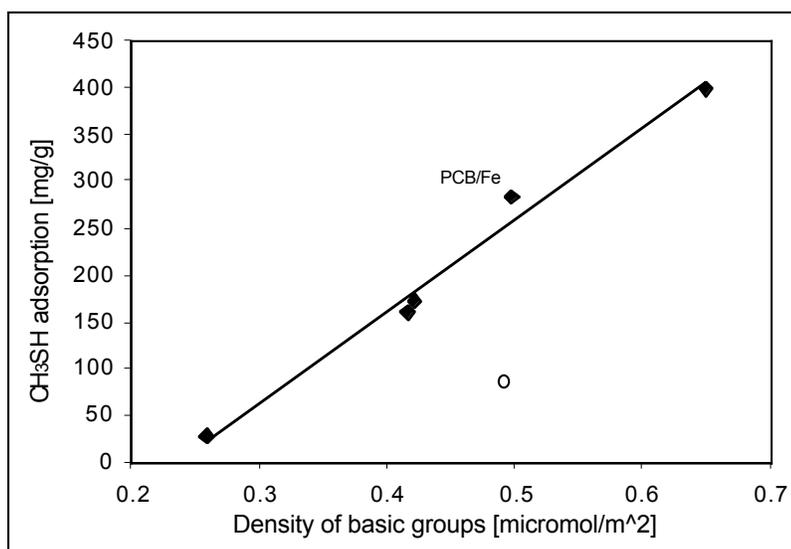


Figure 1. Dependence of MM adsorption capacity on the density of basic groups.

To improve the performance of PCB carbon as MM adsorbent, it was impregnated with iron and subjected to a MM breakthrough capacity test. XRF shows that after the impregnation PCB has the same amount of iron as BPL ($\approx 0.4\%$) and its MM capacity increased more than 3 times from 85.5 mg/g to 284.0 mg/g.

Another important factor link to surface chemistry is carbon pH. It was found that for all

carbons with the average surface pH greater than 7.6 concentration of CH_3S^- in the adsorbed state will be equal to CH_3SH in a gas phase (100% dissociation + adsorption), which is required for effective CH_3SH removal. Although the pH of most of our carbons is less than 7.6, it should be taken into consideration that we measure the pH of the suspension, which can be different from the pH inside the carbon pores. Nevertheless, the smallest pH was found for the BAX carbon, which could be the cause of its poor MM adsorption capacity.

It is clear that different parameters of the carbon surface determine their performance as MM adsorbents, but the process of adsorption cannot be effective without a developed pore structure where the products of adsorption/oxidation have to be stored. S208, PCB and Centaur[®] samples can be characterized as microporous carbons with all the pores smaller than 30 Å. On the other hand, BAX and BPL samples are heterogeneous with a lot of pores in the mesoporous region (20-500 Å). Although BAX carbon has a highly developed porosity and very large surface area its negligible CH_3SH capacity can be due to a small volume of pores smaller than 10 Å and large average micropore size. Structural characteristics of BPL cannot explain its high MM adsorption capacity, indicating that surface chemistry and the presence of iron in particular is a factor governing the adsorption of MM on this carbon's surface. For PCB carbon surface chemistry is a predominant factor as well, its high microporosity does not compensate the lack of catalytically active metals on its surface. Centaur[®] carbon is the only one with all the characteristics needed for efficient MM removal, its catalytic nature is supported by a large relative micropore volume and small size of micropores.

Conclusions

The results of the present work reveal complexity of the process of MM adsorption/oxidation on different carbon samples. The nature of each individual sample is unique and determines its activity for MM adsorption/oxidation. Surface chemistry is very important for the efficient MM removal. The dependence was found between the MM adsorption capacity and the density of basic groups on the surface. However without the presence of catalytically active metals such as iron the adsorption/oxidation process seems to be less effective. pH of the carbon surface is another significant factor. pH threshold value was estimated to be 7.6. Although structural characteristics are not critical factors in this case, the process of adsorption cannot be effective without a developed pore structure and presence of small pores.

References

- [1] Bansal RC, Donnet JB, Stoecki K. Active Carbon, New York: Marcel Dekker, 1988: 119-162.
- [2] Adib F, Bagreev A, Bandosz TJ. Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide. J. Colloid Interface Sci. 1999; 214:407.
- [3] Bashkova S, Bagreev A, Bandosz TJ. Adsorption of mercaptan on activated carbons. Environ. Sci. Technol. 2002;36:2777-2782.

- [4] Bashkova S, Bagreev A, Bandosz TJ. Effect of surface characteristics on adsorption of methyl mercaptan on activated carbons. *Ind. Eng. Chem.* 2002;41:4346-4352.
- [5] Bagreev A, Bashkova S, Bandosz TJ. Dual role of water in the process of methyl mercaptan adsorption on activated carbons. *Langmuir.* 2002;18:8553-8559.
- [6] Kato H, Kuniyoshi I, Hirai M, Shoda M. Studies of the oxidation mechanism of sulfur-containing gases on wet activated carbon fibre. *Appl. Catal. B: Environ.* 1995;6:255.
- [7] Shin CS, Kim KH, Ryu SK. Adsorption of methyl mercaptan and hydrogen sulfide on impregnated activated carbon fibre and activated carbon. Presented at the 7th International Conference of Fundamentals of Adsorption. Nagasaki, Japan, May 20-25, 2001.
- [8] Olivier JP. Modeling physical adsorption on porous and nonporous solids using density functional theory. *J. Porous Mater.* 1995;2:9.
- [9] Boehm HP. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon.* 1994;32:759.