EFFECT OF SURFACE CHARACTERISTICS OF WOOD BASED ACTIVATED CARBONS ON ADSORPTION OF HYDROGEN SULFIDE

*Foad Adib[1], Andrey Bagreev[2], and Teresa J. Bandosz**

*Department of Chemistry and [1]Department of Civil Engineering, The City College of New York and The Graduate School of the City University of New York, and Center for Water Resources and Environmental Research of CCNY; * E-mail: tbandosz@scisun.sci.ccny.cuny.edu*
[2]Permanent address: Institute for Sorption and Problems of Endoecology, Kiev-164, 252180, Ukraine

Introduction

This study present the performance of wood based virgin activated carbons as adsorbents of hydrogen sulfide. Based on the detailed study of surface chemistry and the breakthrough capacity results, the mechanism of H_2S adsorption/oxidation is proposed. The oxidation products are related to the differences in the surface features of wood based carbons.

Experimental

Materials:

Three activated carbons manufactured by Westvaco were used for this study: BAX-1500, WVA-900, and WVA 1100. They are referred to as W1, W2, and W3, respectively. The exhausted carbons after the breakthrough capacity tests are designated as W1-E, W2-E, and W3-E. The materials after washing (removal of water soluble species) are referred to as W1-S. W2-S, and W3-S.

Methods:

H_2S breakthrough capacity test was carried out using moist air containing 0.3 % (3000 ppm) H_2S which was passed through a column of carbon (length 370 mm, diameter 9 mm) at 0.5 L/min to a breakthrough concentration of 500 ppm. The oxygenated surface groups were determined according to the method of Boehm [1]. Thermal analysis of carbons was carried out using a TA Instruments Thermal Analyzer. The concentration of sulfate ion in the leachate was measured by ion chromatography using a Dionex 4500I chromatograph with AS9-SC column. Temperature programmed desorption experiments (TPD) were conducted on a Pulse ChemiSorb 2705 (Micromeritics) using helium as the carrier gas. The content of sulfur in the initial and exhausted carbons was measured by commercial lab. Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at 77 K. Water sorption experiments were carried out at different temperatures close to ambient (283 K-303 K) using Micromeritics ASAP 2010 with vapor sorption kit. FTIR spectra were collected using a Nicolet Impact 410 (DRIFT).

Results and Discussion

The dependence of the hydrogen sulfide breakthrough capacity on the structural parameters and surface chemistry is presented in Table 1. Although the W1 and W3 showed similar capacities for H_2S, the W1 carbon required an intensive prehumidification to reach this level. Since all Westvaco carbons chosen for this study are characterized by very high affinity for water compared to other carbons [2] it was concluded that beyond a certain critical amount of water on the carbon surface the H_2S breakthrough capacity is insensitive to this parameter [3].

Based on the detailed study of surface chemistry and the performances of carbons we suggest that the hydrogen sulfide breakthrough capacity is governed by local pH within the pore system [3]. This local pH depends on the pore sizes and the location of acidic groups. Pores should be large enough to accommodate surface functional groups and small enough to have a film of water at relatively low pressures. Too low a pH results in physical adsorption of H_2S while too high a value leads to high concentrations of dissociated hydrogen sulfide ions and their oxidation to polymeric sulfur. Hydrogen sulfide can be oxidized to sulfur oxides only when atomic sulfur exists in small pores as an intermediate product.

Besides the differences in the performance of W1 and W3 carbons compared to W2 as adsorbents of H_2S, differences in their oxidation products are also expected. The presence of elemental sulfur and sulfur oxides on exhausted carbon surface can be analyzed using thermal methods [4, 5]. Peaks on DTG curves represent the weight loss during heating in nitrogen. In the case of the W1-E and W3-E samples two well defined peaks with maxima at around 500 K and 600 K are revealed. Their relative intensities are different for the two carbons. Since the only "modification" of the sorbents structure was the adsorption/oxidation of H_2S those new peaks must represent the products of oxidation, namely elemental sulfur (at around 600 K) and sulfuric or sulfurous acids (at around 500 K) [4, 5].

The effects of oxidation of hydrogen sulfide on the carbon surface and its regeneration by washing are also investigated using DRIFT. Washing creates differences in

the spectra of all exhausted samples. The most significantly decreased bands are at 580 cm^{-1}, 700 cm^{-1}, 850 cm^{-1}, 950 cm^{-1}, 1050 cm^{-1}, and 1150 cm^{-1} which represent SO_4^{2-} and HSO_4^-.

The detailed analysis of the sulfur content is presented in Table 2 where the percentage of S in the form of sulfuric acid evaluated from ion chromatography is included (S^{6+}(IC)). After washing a decrease in sulfur content is observed for the W1 and W2 samples, as expected from TA analysis. The yield of oxidation was calculated from the percentage of sulfur in higher oxidation states. The results indicate that around 30% of sulfur in the case of the W2 sample was oxidized to soluble sulfur oxides. In the cases of W1 and W3 the yield of soluble S^{4+} and S^{6+} were 21% and 13%, respectively.

Conclusions

The results show significant contribution of the local pH (in the pores of carbon) to oxidation of hydrogen sulfide. Although the yield of water soluble species is much higher when the carbon surface is very acidic, the total sorption capacity is very low. Only a slight increase in an average pH (half a unit) results in more than a fifteen fold higher capacity, owning to the dissociative adsorption of hydrogen sulfide ions and their oxidation, with only one third decrease in the yield of water soluble sulfur species.

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Table 1. H_2S breakthrough capacity, structural parameters and the results of the analyses of surface chemistry.

Sample	H_2S breakth. capacity [mg/g]	S [m^2/g]	V_{mic} [cm^3/g]	g all groups [group/nm^2]	γ acidic [group/nm^2]	# of groups (TPD) [mmol/g]	CO/ CO_2 (TPD)
W1	295	1400	0.561	0.531	0.477	5.67	5.8
W2	17	1025	0.359	0.792	0.734	3.93	4.7
W3	230	1110	0.410	0.739	0.562	3.91	5.4

Table 2. pH carbon and sulfur balance: S_t (A) - sulfur content measured in the analytical laboratory; S_t- sulfur content evaluated from the breakthrough capacity; S^{+6} (IC) - percentage of sulfur oxidized to S^{+6} evaluated using ion chromatography; S^{ox} (TA) - percentage of sulfur released as SO_2 (water soluble) during heating in nitrogen; S° (TA)- percentage of elemental sulfur evaluated as the weight loss between 550-700 K. Yield is obtained by dividing S^{ox} by S_t

Sample	pH	S_t (A) [%]	D S_t after washing [%]	S_t calc. after Bth.test [%]	S^{+6} (IC) [%]	S^{ox} (TA) [%]	S° (TA) [%]	Yield S^{ox}/ S_t [%]
W1	4.41	<0.5	—	—	—	—	—	—
W2	4.04	<0.5	—	—	—	—	—	—
W3	5.61	<0.5	—	—	—	—	—	—
W1-E	1.76	13.78	—	20.6	1.7	4.3	13.4	21
W2-E	3.00	1.57	—	1.6	0.3	0.2	0.7	31
W3-E	2.04	18.04	—	17.9	1.2	2.4	10.7	13
W1-S	2.61	12.96	6	—	—	1.4	6.5	–
W2-S	4.10	1.25	20	—	—	0.2	0.8	–
W3-S	2.85	15.21	16	—	—	0.8	6.6	—