Adsorption of Hydrogen Sulfide onto Activated Carbon Fibers: Effect of Pore Structure and Surface Chemistry

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To understand the nature of H_2S adsorption onto carbon surfaces under dry and anoxic conditions, the effects of carbon pore structure and surface chemistry were studied using activated carbon fibers (ACFs) with different pore structures and surface areas. Surface pretreatments, including oxidation and heat treatment, were conducted before adsorption/desorption tests in a fixed-bed reactor. Raw ACFs with higher surface area showed greater adsorption and retention of sulfur, and heat treatment further enhanced adsorption and retention of sulfur. The retained amount of hydrogen sulfide correlated well with the amount of basic functional groups on the carbon surface, while the desorbed amount reflected the effect of pore structure. Temperature-programmed desorption (TPD) and thermal gravimetric analysis (TGA) showed that the retained sulfurous compounds were strongly bonded to the carbon surface. In addition, surface chemistry of the sorbent might determine the predominant form of adsorbate on the surface.

Introduction

Hydrogen sulfide is a pollutant that is commonly regarded as toxic. Inhalation of high concentrations of hydrogen sulfide can be lethal (*1, 2*). Hydrogen sulfide mainly attacks the neural system and important organs, like the liver and the kidney (*3–5*). Many industrial processes generate significant quantities of hydrogen sulfide. These processes include natural gas processing, petroleum refining, petrochemical plants, Kraft mills, coke ovens, and coal gasifiers. H_2S concentrations in these processes vary from 0 to 60 vol % (*6*).

The Claus process is used to control gas streams with high concentrations of hydrogen sulfide. Since it can only recover about 95–97% of the hydrogen sulfide, emissions from Claus units are now becoming a source of H_2S pollution. Typical tail gas from Claus plant is at 100–315 °C and still contains about 0.8% to 1.5% H_2S with other gases such as COS, CS_2, and CO_2 at various concentrations. Now Claus plants are required to reduce H_2S emissions from the tail gas (*7*).

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Adsorption/oxidation by carbonaceous surfaces was widely studied as a method to control H_2S pollution. However, there are still some inconsistencies in the literature even on basic questions, including the nature of H_2S adsorption and the role of oxygen-containing surface functionalities. Some researchers reported that physical adsorption is the dominant mechanism for H_2S uptake by carbon materials. If the adsorption occurs under vacuum and in the absence of surface functional groups, the micropore filling theory (*8, 9*), which describes the enhanced physisorption by adsorbent atoms closely surrounding the adsorbate due to small pore size, can explain the adsorption isotherms very well. Boki and Tanada (*10*) studied the adsorption of H_2S onto activated carbon surface at three different temperatures using a vacuum system. The Dubinion–Astakhov equation can be applied to describe the adsorption isotherm. Extraordinarily high isosteric heat of adsorption of one of the carbon used was explained by the small pore size. The authors observed that a small amount of H_2S that was chemisorbed decreased with the decrease in temperature. Aranovich and Donohue (*11*) compared experimental adsorption isotherms for different adsorbates onto microporous adsorbent with those predicted using Dubinin–Radushkevich (DR) equation. They found that the adsorption of H_2S follows the pore filling mechanism. Lee et al. (*12–14*) used a gravimetric adsorption apparatus to study adsorption of hydrogen sulfide and also concluded that it can be explained by the micropore filling theory.

Bagreev et al. (*15*) studied the sorption of hydrogen sulfide on virgin and oxidized activated carbons and reported a good correlation between the heat of H_2S adsorption and the characteristic energy of nitrogen adsorption calculated from the Dubinin–Raduskevich (DR) equation. These results indicate that the adsorption of H_2S under dry and anaerobic conditions is mainly physical and that surface functionalities exhibit no impact on the adsorption process. Similar studies with 15 different activated carbons showed that lower average pore size leads to stronger interaction between H_2S and the carbon surface, which is due to the increase in adsorption potential (*15*).

All of these studies agree that physical adsorption of H_2S dominates under ideal conditions (vacuum, dry, anaerobic, low temperatures). Studies conducted under realistic process conditions (higher temperature, with the presence of other gases such as oxygen, and functionalized surfaces) revealed that chemical adsorption was important and unavoidable. Bandosz (*16*) summarized that activated carbons as hydrogen sulfide adsorbents under field conditions required proper combination of surface chemistry and carbon porosity; more acidic environment promotes the formation of high-valent sulfur compounds and decreases the H_2S removal capacities. A basic environment favors the formation of elemental sulfur and increases sulfur removal capacity. Also, preadsorbed water will enhance hydrogen sulfide dissociation and removal from the gas stream.

Several studies (*16–18*) found that the surface area and pore volume are not the only factors contributing to H_2S adsorption. Surface treatment using ammonia or nitric acid can result in significant change in H_2S removal capacities. Mikhalovsky and Zaitsev (*19*) showed that H_2S adsorption from an inert atmosphere on activated carbons resulted in the formation of surface oxygen-containing complexes and elemental sulfur, thereby suggesting that the adsorption of hydrogen sulfide on carbon surface was dissociative. Cal et al. (*20, 21*) conducted systematic experimental studies with virgin and modified activated carbons at 550 °C and showed
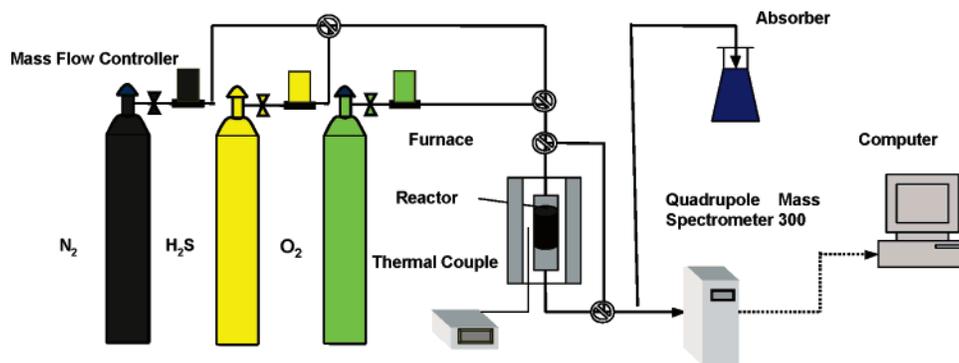
FIGURE 1. Experimental setup for H₂S adsorption/oxidation.

that both HNO_3 oxidation and Zn impregnation improved H_2S adsorption capacity.

Since modification of surface chemistry is likely to be effective for improving H_2S removal capacity by activated carbons, different impregnates were studied. Bagreev et al. (22) evaluated the effect of NaOH on adsorption of H_2S and found that the H_2S removal capacities were dominated by the presence of NaOH and were not sensitive to surface area and pore structure. Other reports on NaOH (23, 24) or K_2CO_3 (25, 26) impregnation also showed significant improvement in the H_2S removal capacity. It is believed that presence of alkaline chemicals facilitates the dissociation of H_2S on carbon surfaces. Pieplu et al. (27) suggested that there are two modes of H_2S adsorption onto surfaces of the catalysts: dissociative and nondissociative. The dissociative adsorption may be due to the interaction between H_2S and $-OH$ group or cations, such as Na^+, Al^{3+}, and Ti^{4+}.

The above literature review revealed that both physical and chemical adsorption could occur during H_2S removal by carbon materials; both surface chemistry and pore structure are important for H_2S adsorption/removal. The nature of H_2S adsorption onto carbonaceous surfaces is still not very clear. It seems the relative contributions of the two parameters mainly depend on the experimental conditions. Only when the functionalities are significantly removed or reaction conditions are ideal, the effect of pore structure is obvious and physical adsorption is dominant. For physical adsorption, smaller pore size can exert stronger interaction between H_2S and carbon according to the micropore filling theory. However, under realistic process conditions, carbon surface chemistry is very important.

The objective of this study was to investigate the effect of pore structure and surface chemistry on hydrogen sulfide adsorption and to understand the nature of hydrogen sulfide adsorption onto carbon surface under dry and anoxic conditions (in a pure nitrogen stream). Raw ACFs before and after surface treatment (heat treatment and oxidation) were characterized to determine the impact of pore structure and surface chemistry on their adsorption properties. Additional insights into the fundamentals of H_2S adsorption were obtained from temperature-programmed desorption studies and surface characterization of saturated sorbents.

Experimental Section

Activated Carbon Fibers. The carbonaceous sorbents selected for this study were activated carbon fibers (ACFs), which have fairly uniform pore size distributions. ACFs with carbon content of over 95% were obtained from American Kynol, Inc. ACFs were produced from the novolac resin that is manufactured by polymerization of phenol and formaldehyde. Detailed information about the surface properties and structure of this sorbent is available in the literature (28). ACF10, ACF20, and ACF25 were produced using increasing activation time, which leads to higher surface area and larger pores. With the increase in serial number, the nominal surface area and average pore size increased. According to the previous study (29), ACF10, ACF20, and ACF25 have relatively narrow pore size distribution with average pore widths of 7.1, 7.8, and 9.7 Å, respectively.

Sample Preparation. The ACFs were dried at 120 °C for 2 h and mechanically ground into powder prior to any further treatment. A 1 g amount of powdered ACF was loaded into the fixed bed reactor for each hydrogen sulfide adsorption/oxidation experiment. Different methods were applied to modify the carbon surface: "Dried" samples were dried in nitrogen at 140 °C for 2 h, "heat-treated" samples were heated in nitrogen to 900 °C at 200 °C/h, maintained at 900 °C for 4–6 h, and then cooled to room temperature at 200 °C/h, and "oxidized" samples were first dried and then heated to 200 °C for 2 h in a pure O_2 stream. "Heat-treated" samples were denoted by the carbon material, heat treatment temperature, and heat treatment duration. For example, ACF10-900C-4h denotes raw ACF10 that was treated at 900 °C for 4 h.

Experimental System and Procedure. Figure 1 shows the fixed bed reactor system used for H_2S adsorption studies. The gases were supplied by pressurized tanks. For H_2S adsorption, standard H_2S gas of 200 ppm in nitrogen (certified grade, Praxair, Danbury, CT) was used for adsorption test. Higher concentrations of H_2S were generated by diluting 5% H_2S standard gas (certified grade, Praxair, Danbury, CT) with nitrogen (ultrahigh purity, Praxair, Danbury, CT). Mixed gas with a total flow rate of 150 mL/min was fed through a quartz reactor (38 cm long with 1 cm o.d.), which was positioned vertically in the middle of a tubular furnace (Lindberg Heavi-Duty, Watertown, WI) with a temperature controller. The effluent gases were analyzed continuously by a QMS 300 (quadrupole mass spectrometer 300, Stanford Research Systems, Sunnyvale, CA). The adsorption and desorption experiments were conducted at 23 °C unless specified otherwise.

Immediately after the pretreatment of the ACFs in the fixed bed reactor, the reactor was first flushed with pure N_2 for 30 min and the inlet gas was switched to gas mixture with desired H_2S concentration and the data collection was initiated. The H_2S concentration was continuously monitored by QMS until saturation was reached. After saturation, the inlet gas was switched back to pure N_2 and the H_2S concentration desorbed from the carbon surface was recorded continuously. The "adsorbed amount" can be obtained by integrating the area above the breakthrough curve. The "desorbed amount" can be obtained by integrating the area below the desorption curve. The difference between adsorbed amount and desorbed amount is defined as the "retained amount".

Analysis. Surface Area and Pore Structure Analysis. The surface area and pore size distribution of ACFs were analyzed using nitrogen adsorption at 77 K in a Quantachrome

TABLE 1. Micropore Structure of ACFs before and after Heat Treatment

	pore volume (cm³/g)				surf area (m²/g)
samples	small pores (4.0−7.2 Å)	medium pores (7.2−9.0 Å)	big pores (>9.0 Å)	tot. (>4.0 Å)	
ACF10-raw	0.274	0.039	0.065	0.378	920
ACF20-raw	0.258	0.104	0.329	0.691	1453
ACF25-raw	0.263	0.101	0.489	0.853	1920
ACF10-900C-4h	0.291	0.069	0.112	0.472	965
ACF25-900C-6h	0.276	0.095	0.554	0.925	1964

Autosorb automated gas sorption system (Quantachrome Corp., Boynton Beach, FL).

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was conducted using TGA7 (Perkin-Elmer, Norwalk, CT) where the sample was maintained at 120 °C for 2 h and then heated to 850 °C with a heating rate of 10 °C/min in an ultrahigh-purity nitrogen atmosphere.

Temperature-Programmed Desorption. After adsorption and desorption in nitrogen at 23 °C, the temperature of the tubular furnace was raised at 600 °C/h (10 °C/min) up to 900 °C and effluent gas was monitored with QMS. Atomic mass units (amu's) of interest and the desorption temperatures were recorded continuously. During TPD, the carrier gas flow rate was 15 mL/min.

Sulfur Analysis. Sulfur analysis was conducted using a Leco model SC-132 Sulfur Determinator (Leco Co., St. Joseph, MI). The furnace temperature was first raised to 1200 °C, and a ceramic boat containing about 100 mg of sample was placed inside the furnace. Sulfur content was obtained on the basis of calibration with the standard sample (Leco Co., St. Joseph, MI) of known sulfur content (3.11% ± 0.06%).

Boehm Titration. The Boehm titration was conducted according to Boehm (30, 31). Titration procedure refers to the ASTM method (Method 2310B and 2320B). ACF samples were soaked in standard acid or base solutions for 24 h. The amount of different acidic surface functionalities and the total amount of basic functionalities can be determined on the basis of the following assumptions: 0.25 N NaOH neutralizes total acidity; 0.05 N NaOH neutralizes carboxyl, phenolic, and lactonic groups; Na_2CO_3 neutralizes phenolic and lactonic groups; $NaHCO_3$ only reacts with phenolic groups.

Results

Characterization of ACFs. Table 1 summarized the surface area and pore volume of ACFs before and after heat treatment, while Figure 2 shows the pore size distribution of selected samples. On the basis of these results, the pore size of raw ACFs was divided into three ranges corresponding to three peaks consistently shown in the pore size distribution figures. The pore volume of each region was obtained from the BET analysis results and is listed in Table 1.

With the increase in serial number of raw ACFs (from ACF10 to ACF25), both surface area and pore volume increased, which is consistent with the manufacturer's specifications. After heat treatment at 900 °C for 4 h (sample ACF10−900C-4h), the pore volume and surface area of ACFs increased very slightly, which may be due to the release of adsorbed species or the expansion of pores because of additional volatilization of ACFs. Another explanation is the reaction between active gases with the ACFs to form higher surface area and bigger pore volume. Although present in very limited amount (<3 ppm), oxygen from the ultrahigh-purity (UHP) nitrogen gas stream may contribute to the surface area and pore volume increase. Similar results were also reported by Daley et al. (32); they concluded that heat treatment has almost no effect on the pore structure of ACFs.
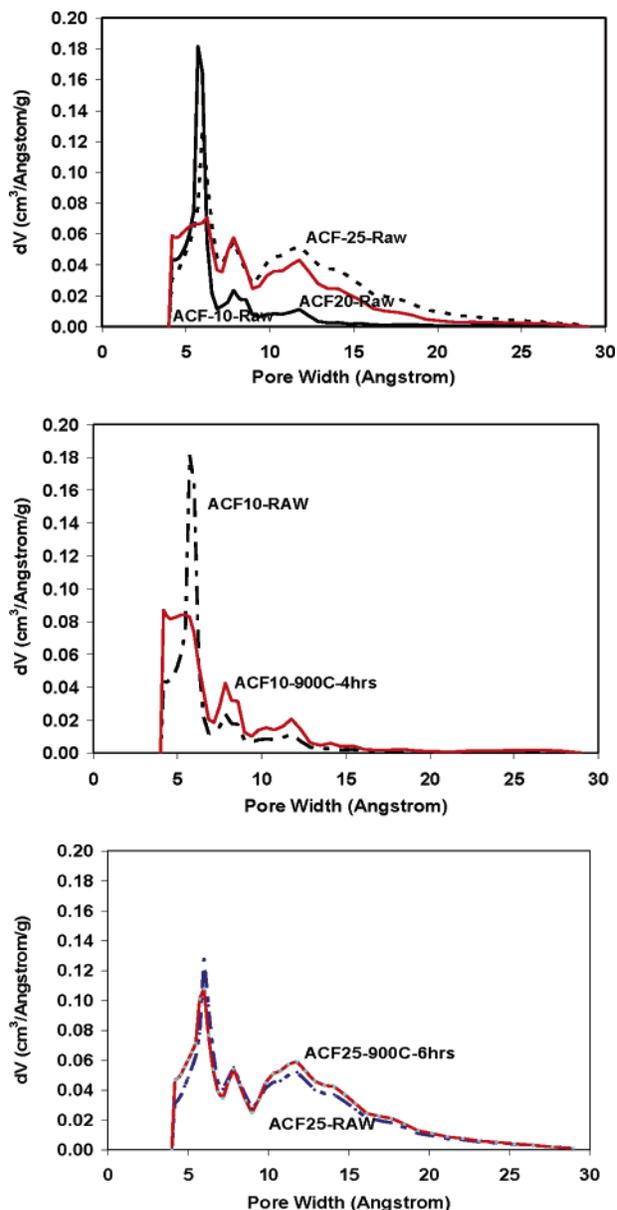

FIGURE 2. Pore size distribution of selected ACFs before and after heat treatment.

Analysis of the pore volume change in different ranges shows that higher serial number of ACF has higher portion of bigger pores. From ACF10 to ACF20, there is a significant increase in both medium and big micropores as a result of longer activation, but the small micropore volumes did not change significantly. From ACF20 to ACF25, the pore volume increase is mainly due to the increase in big micropores. Figure 2a also shows that, with the increase in serial number, the pore size distribution becomes less uniform in all ranges. The same behavior was obtained after heat treatment in this study (as shown in Figure 2b,c) because the heat treatment increased mainly the medium and big micropores for ACF10 and only big micropores for ACF25.

Table 2 summarizes the surface functionalities obtained through Boehm titration. The total acidic surface functionalities decreased with an increase in serial number. However, the total amount of basic functional groups increased with the increase in serial number. The basicity on carbon surfaces is reported to be associated with functional groups, such as pyrone, chromene, diketone, or quinone groups (33). Also, the increase in the density of graphitic platelets carrying π

TABLE 2. Surface Functionalities on Raw ACFs Determined by Boehm Titration (mmol/g)

ACF no.	tot. acidic	carbonyl	carboxyl	lactonic	phenolic	tot. basic
ACF10	3.11	2.42	0.348	0.037	0.309	0.439
ACF20	2.70	2.04	0.326	0.068	0.270	0.670
ACF25	2.09	1.43	0.309	0.079	0.273	0.790

TABLE 3. Adsorbed, Desorbed, and Retained Amount (mg/g) of H_2S by ACFs before and after Different Surface Treatments

surf treatment		ACF10	ACF20	ACF25
raw (dried)	adsorbed	1.43	2.18	2.65
	retained	0.37	1.29	1.77
	desorbed	1.06	0.89	0.88
oxidized	adsorbed	1.96	3.62	4.57
	retained	0.86	2.71	3.77
	desorbed	1.1	0.91	0.8
heat treated	adsorbed	1.61	2.74	3.86
	retained	0.57	2.14	3.34
	desorbed	1.04	0.6	0.52

FIGURE 3. N_2 isotherms at 77 K for raw ACFs.

FIGURE 4. Adsorbed and retained amount of H_2S on ACFs/unit surface.

electrons during extended activation might contribute to the increase in basicity.

Effect of Pore Structure and Surface Treatment on H_2S Uptake. Raw ACFs before and after surface treatment (oxidation at 200 °C and heat treatment in nitrogen at 900 °C) were subjected to H_2S adsorption/desorption tests. The H_2S adsorption experiments were carried out at room temperature, with 200 ppm H_2S in pure nitrogen. Table 3 summarizes test results. As mentioned above, the adsorbed amount was divided into retained amount and desorbed amount. The latter one is the amount desorbed in nitrogen. The desorbed amount can be viewed as physically adsorbed, while the retained amount can be viewed as chemisorbed.

Table 3 shows that regardless of the surface treatment, with the increase in serial number of the ACFs, the adsorbed and retained amount of H_2S increased. According to the sorbent characterization shown in the previous section, the surface area, pore volume, average pore size, and total basic functionalities increased with the increase in serial number of ACFs. Considering the fact that retained amount could not be easily removed from the carbon surface, it is believed that the increase in the retained amount is mainly due to the change in the amount of active sites that may be related to surface area.

The desorbed amount decreased with the increase in serial number. However, the decrease in desorbed amount (about 1 mg/g for all cases) is not significant compared with the increase in retained amount. A slight decrease in desorbed amount with the increase in serial number can be qualitatively explained by the micropore filling theory (8, 9), which predicts that pores of smaller size will adsorb more adsorbates at lower concentrations due to the higher adsorption potential exerted by their walls. Figure 3 shows the N_2 adsorption isotherms of raw ACFs at 77 K. Indeed, at a relative pressure (p/p_0) of 1.2×10^{-5}, there is a crossing point, below which ACF10 has higher adsorption capacity than ACF25. Although the average pore size increased with the increase in serial number, the micropore volume did not change significantly, leading to relatively small changes in desorbed amount (Table 1).

Table 3 consistently shows that both oxidized and heat treated ACFs have higher adsorbed and retained amount than the raw ACFs (dried), with oxidized ACFs achieving the highest retention of hydrogen sulfide. Oxidation at low temperature (200 °C) is not likely to change the pore structure. It can, therefore, be concluded that surface chemistry
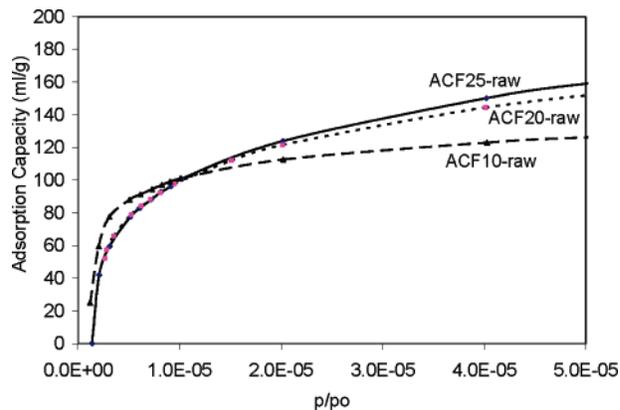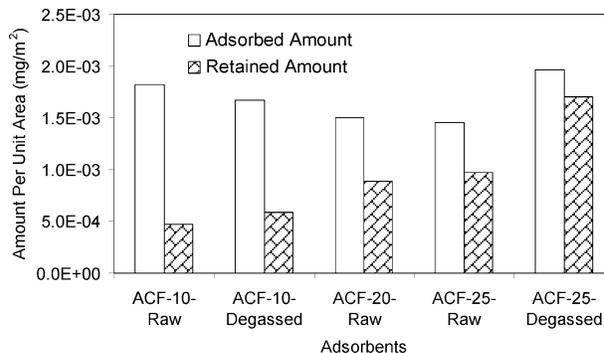
contributed more to this phenomenon. Oxidation obviously increases the surface oxygen containing functionalities, which may be one form of the active sites for H_2S uptake. The amount of H_2S retained on the ACF surface was likely oxidized by, or strongly bonded to, these surface functionalities. Bouzaza et al. (34) observed that oxidation of H_2S occurred even if the gaseous oxygen was not present in a dry atmosphere. They concluded that the oxidation is due to the oxygen-containing surface functionalities of the carbon fibers.

The increased H_2S uptake by heat treated ACFs can also be explained by the change in surface chemistry. It is commonly believed that heat treatment under inert environment will decrease and even totally eliminate the surface oxygen containing functionalities without changing the pore structure. However, it is reported (35) that the removal of oxygen during high-temperature N_2 treatment leaves unsaturated carbon atoms at crystallite edges, which lead to very high heat of adsorption during adsorption of oxygen. Since the retained amount increased after heat treatment, these unsaturated sites are likely responsible for H_2S uptake.

The adsorbed and retained amounts per unit pore volume or per unit surface area can be calculated using the data shown in Tables 1 and 3. All the data were obtained at 23 °C. The results in terms of surface area depicted in Figure 4 clearly show that the retained amount/unit surface area of raw (virgin) ACF increased with the increase in surface area. ACFs with higher serial numbers were produced after longer activation times, leading to an increase in both surface area and oxygen-containing active sites/unit surface area. If the surface area alone were responsible for increased retention of H_2S, the retained amount/unit surface area should remain constants for all ACFs. However, Figure 4 clearly shows that the retained amount/unit surface area changed from one ACF to another. It can, therefore, be concluded that the surface chemistry is more important for H_2S chemisorption. The retained amount of H_2S/unit surface area increased after
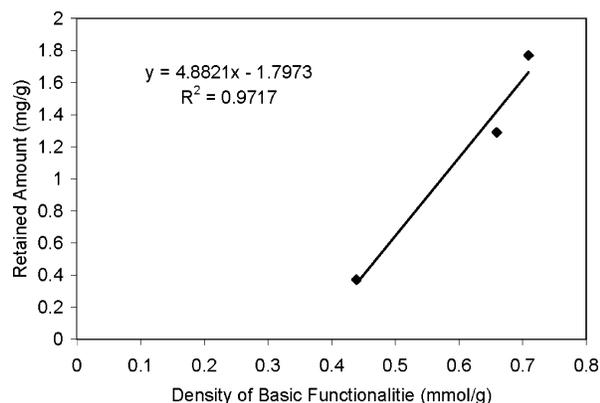
FIGURE 5. Correlation of basic surface functionalities with H_2S retention (chemisorption) for raw ACFs.

heat treatment (ACF10-raw vs ACF10-900C-4h and ACF25-raw vs ACF25-900C-6h), which can be explained by the increase in the amount of unsaturated active sites. The desorbed amount, which is the difference between adsorbed and retained amount, decreased with the increase in pore volume and pore size, which can be explained in terms of micropore filling theory.

Surface basic functionalities represent possible active sites that are responsible for H_2S retention through acid/base interactions. The amount of basic functionalities detected by Boehm titration was correlated with the retained amount on raw ACFs in Figure 5. Strong linear correlation between the basic surface functionalities and the amount of H_2S retained by raw ACF is not unexpected because H_2S is an acidic gas. Bashkova et al. (36) reported a strong correlation between basic functionalities and adsorption of methyl mercaptan, which also revealed the importance of acid−base interactions in acidic gas adsorption.

Temperature-Programmed Desorption. Temperature-programmed desorption (TPD) reveals possible interactions between adsorbed H_2S and carbon surface because higher desorption temperature reflects stronger bonding. The effluent during TPD experiments was monitored at specific amu's, namely 16 (O), 28 (CO or N_2), 32 (S or O_2), 34 (H_2S), 44 (CO_2), 64 (S_2 or SO_2), and 76 (CS_2).

Figure 6a shows the TPD profiles for raw ACF10 after adsorption of 3000 ppm H_2S followed by desorption in nitrogen. The desorption in nitrogen was carried out for 24 h to ensure that all reversibly adsorbed sulfur species were removed. Figure 6a shows that most sulfur species were released between 260 and 450 °C. TGA test also shows that most of the weight loss occurred between 220 and 420 °C for raw ACF10 after adsorption and desorption at 23 °C. According to Pieplu et al. (27), the dissociatively adsorbed H_2S desorbed at 290−315 °C. Among the sulfur-containing species, SO_2 was released first, while COS was released at slightly higher temperatures. Figure 6b shows that a trace amount of O_2 was released around 160 °C. Virgin sorbent has oxygen content around 5%, which is the most probable source of O_2 because ultrahigh purity of N_2 was used as the carrier gas. The results in Figure 6 indicate that H_2S was strongly bonded to the carbon surface and that most of the H_2S was probably oxidized by oxygen (at the carbon surface) during the adsorption process or during the TPD run. Figure 6b shows that there was sufficient amount of oxygen on the ACFs surface for complete H_2S oxidation because CO_2 desorption was still observed at temperatures above 200 °C (37, 38).

Sulfur analysis shows that indeed there is a significant amount of sulfur retained on the carbon surface after nitrogen desorption and that some sulfur remained on the carbon surface even after exposure to 850 °C (data not shown). The
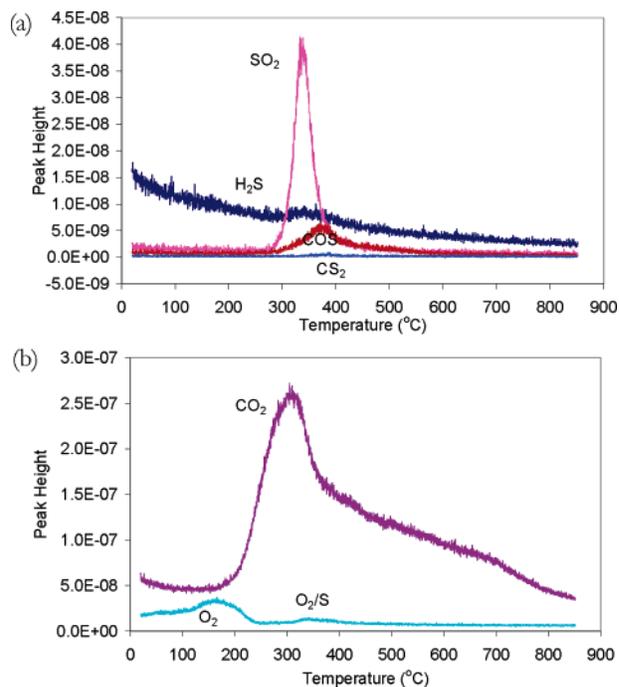

FIGURE 6. Gas species released during TPD of ACF10-raw: (a) sulfur-containing species; (b) other species.
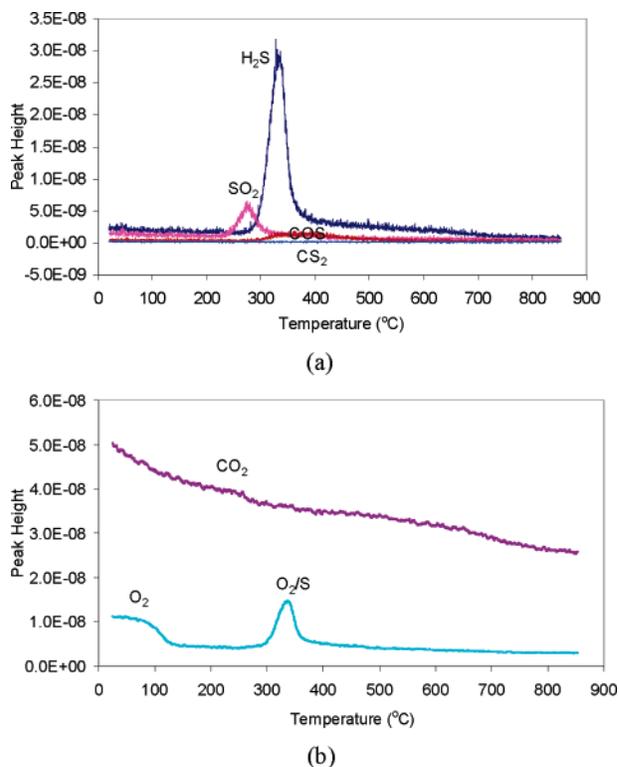

FIGURE 7. Gas species released during TPD of ACF10-900C-4h: (a) sulfur-containing species; (b) other species.

sulfur that remained after TPD run may have been imbedded deeply into the carbon structure during the heating process.

Figure 7 shows TPD profiles for heated-treated ACF10 (ACF10-900C-4h) after adsorption of 3000 ppm H_2S and desorption in nitrogen. In contrast to the results obtained for raw ACF10 (Figure 6), the major sulfur species desorbed in the effluent was H_2S, while small amount of SO_2 was released at lower temperatures (Figure 7a). Another major difference is that there was no significant amount of CO_2

evolving from heat treated ACF10 (Figure 7b). Such behavior was expected because most of the surface oxygen was removed during sample pretreatment. These results show that the sulfur species can be strongly bonded to the carbon surface even when most of the oxygen was removed from the surface. In that case, the majority of the sulfur species were present on the carbon surface in the reduced form. The results in Figures 6 and 7 show different pathways responsible for the increase in the retained amount of H_2S for raw and heat treated samples (Table 3). For raw ACF10, the presence of oxygen promotes the oxidation of H_2S, as reported by previous researchers (19, 34). For heat-treated ACF10, the decomposition of oxygen-containing functionalities creates unsaturated basic sites (35) or liberated π-electrons associated with basal planes, thereby promoting the retention of H_2S mainly through acid−base interactions.

Acknowledgments

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