

OXIDATION OF HYDROGEN SULFIDE OVER MICROPOROUS CARBONS

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Abstract—Microporous carbon of high purity was produced by the carbonization of Saran at 900° followed by activation in either CO₂ at 900°, O₂ at 300°, or air at 425°. The activated carbons were characterized using N₂ adsorption at -195°, CO₂ adsorption at 25°, and mercury and helium displacements. Hydrogen sulfide oxidation (at H₂S pressures between 0.4–3.8 Torr) by O₂ (in excess of stoichiometric amount) was studied between 100–160° using a microbalance, that is by weighing the build-up of sulfur on the carbon. The predominant reaction, $H_2S + \frac{1}{2} O_2 \rightarrow \frac{1}{2} S_2 + H_2O$ was first order in H₂S concentration and independent of O₂ concentration. The rate was only slightly reduced by sulfur build-up to at least 36%, by weight, on the carbon. The oxidation rate was significantly higher over the O₂-activated carbon than over the CO₂-activated carbon. Throughout the studies, oxidation rates could be correlated with area active to O₂ chemisorption. It is concluded that H₂S oxidation proceeds *via* rapid dissociative chemisorption of oxygen on carbon sites followed by reaction with H₂S. Rates of H₂S oxidation were also studied over commercial, granular activated carbons of significant ash contents.

1. INTRODUCTION

One method that has been proposed to treat low-concentrations of H₂S as encountered in waste gas streams is its selective oxidation to elemental sulfur over an activated carbon catalyst at about 150° [1, 2]. Sulfur recovery appears promising as the sulfur deposited on the carbon can be easily removed using solvent extraction or steam distillation. Activated carbons prepared from coal and coconut shells have been used to catalyze H₂S oxidation. However, it is known that such carbons contain appreciable amounts of impurities which are derived from the mineral matter content inherent in the raw materials. The main impurities, silica, alumina, iron oxide, calcium oxide, and magnesia, might be good catalysts. Therefore, there is a question as to whether the impurities are the catalysts and the carbon is in essence acting as a support or whether, indeed, the carbon surface has significant catalytic activity.

In this study carbons of high surface area and high purity were produced by carbonization of Saran and then activation of the resultant chars. Their catalytic activity for the oxidation of H₂S was measured and compared with the activities of granular, commercial activated carbons of significant ash content.

2. EXPERIMENTAL

2.1 Materials

Saran 489, supplied by the Dow Chemical Company, was used as the precursor in this study. This Saran is a co-polymer of vinylidene chloride and vinyl chloride in an approximate mole ratio of 90:10. A 25 lb sample was slowly heated to 900° and held at this temperature for 4 hr in a flowing dry, high purity N₂ stream. Under these conditions chlorine is liberated stoichiometrically as HCl, leading to the production of a microporous char [3, 4]. The char was ground, with 28 × 48, 65 × 150 and 150 × 250 mesh sizes used in this study.

The H₂S used for the oxidation study was obtained

from Matheson Gas Products, Inc. It was diluted with helium to a concentration of 0.502%; this concentration is typical of that found in flue gas.

2.2 Characterization of microporous carbons

A standard volumetric adsorption apparatus was used to measure N₂ uptake at -195° and CO₂ uptake at 25°. Surface areas were calculated from N₂ adsorption using the BET equation [5] and from CO₂ adsorption using the Dubinin equation [6]. Molecular areas used for N₂ and CO₂, at adsorption temperatures, were 16.2 and 25.3 Å², respectively.

Mercury densities and macropore volumes were determined using an Aminco laboratory porosimeter. Mercury density was measured from mercury displacement by the sample under a pressure of 75 psi. The sample macropore volume was that volume filled by mercury under a pressure of 7000 psi, which is equivalent to a pore diameter of 300 Å.

The apparatus used to determine sample density by helium displacement was a constant pressure type, thermostated to operate at 32.5° ± 0.1°.

2.3 Activation of Saran carbon

Activation was conducted in a silica glass fluid bed reactor, 50 mm o.d. and 80 cm long. The reactor and auxiliary equipment are described in detail elsewhere [7]. Activation was conducted at atmospheric pressure in CO₂ at 900°, O₂ at 300° and air at 425°. Under these conditions, rates of carbon burn-off (to produce activation) were closely similar.

Samples of carbonized Saran were air-dried at 105° in a separate oven prior to activation. Approximately 25 g samples were introduced into the pre-heated reactor under a flowing stream of N₂ and allowed to reach reaction temperature prior to introducing the activating gas. Following activation for the desired time, the sample was cooled in the reactor under N₂. The activated sample

was removed from the reactor and re-weighed to determine weight loss (defined as carbon burn-off) due to gasification.

2.4 Hydrogen sulfide oxidation

Oxidation of H_2S was followed gravimetrically by measuring the weight of sulfur depositing on the carbon. At the end of selected runs, sulfur contents on the carbon were also analyzed chemically using a Leco Sulfur Analysis Apparatus.* Agreement between the two approaches was within 5% in all cases.

A Cahn RG electrobalance, having a total capacity of 2.5 g and a sensitivity of 0.1 μ g, was used to follow continuously sample weight change. Weight change read-out was monitored directly on a 1 mV recorder. The microbalance, housed in a glass vacuum bottle, was connected to a mercury diffusion-mechanical pump combination in order to attain a running vacuum of 10^{-5} Torr. A Vycor glass tube, 27 mm o.d. and 65 cm long, was connected to the microbalance housing and served as the reactor. The carbon sample was held on a cylindrical fused quartz pan, 10 mm dia. by 15 mm high, which in turn was suspended into the reactor from the balance by a 4 mil dia. Vycor wire. Generally, a 125 mg sample was used in the studies. Temperature was monitored and controlled using a chromel-alumel thermocouple located at the outside wall of the reactor tube and connected to a Westbend type temperature controller.

Generally, prior to an oxidation run the carbon sample was heated to 900° under vacuum to remove most of the oxygen complex held on the surface. At reaction temperature, O_2 was first dosed into the reactor at a pressure (usually 7.6 Torr) which would give an O_2 - H_2S ratio of 2 to 1. Immediately thereafter sufficient pre-mixed H_2S in He was added to attain a total pressure of 1 atm. Since the concentration of H_2S in He was 0.5%, the H_2S partial pressure was close to 3.8 Torr. An oxidation run could be monitored within 2 min of the first introduction of O_2 into the reactor. Most runs were carried out for about 5 hr. During this period, the decrease in H_2S pressure because of oxidation was less than 10%. Following a run, sulfurized carbons could be outgassed at temperatures up to 160° with no detectable change in weight, provided a nitrogen cold finger was located between the mercury diffusion pump and the reactor [8].

*Obtained from Laboratory Equipment Corp., St. Joseph, Michigan.

3. RESULTS AND DISCUSSION

3.1 Nature of porosity in Saran carbons

Tables 1 and 2 summarize surface area and pore volume results, respectively, for the carbonized Saran carbon (of 150×250 mesh particle size) and samples activated in different oxidizing gases. The effect of activation of Saran carbon in CO_2 on surface areas as measured by N_2 and CO_2 is similar to that reported previously by Lamond and Marsh [9]. That is, the N_2 area increases monotonically with increasing burn-off; whereas the CO_2 area essentially remains unchanged. Samples activated in air and O_2 also have N_2 areas significantly larger than the CO_2 areas. High N_2 areas are thought to be largely fictitious [9]. Micropore areas, as given by CO_2 adsorption, are closely comparable for the CO_2 and O_2 -activated samples but are clearly lower for the samples activated in air to high burn-offs.

Total accessible pore volumes, as calculated from the differences in the reciprocal of the mercury and helium densities, are given in Table 2. Also given are the macropore volumes, as measured by mercury penetration, for voids larger than 300A in dia. As expected, pore volumes increase sharply with increasing burn-off, with the macropore volume contributing in all cases less than 10% to the total pore volume. At comparable burn-offs the total pore vol. generated by CO_2 activation is greater than that generated by O_2 or air activation. This is attributed to a more uniform gasification rate in the radial direction within the particles for CO_2 activation, as discussed elsewhere [7].

3.2 Kinetics of H_2S oxidation over Saran carbons

3.2.1 Long time runs. Unless otherwise mentioned, oxidation runs were carried out at 140° over 150×250 mesh material. Long time runs were conducted on the O_2 -activated Saran sample to determine the effect of significant depletion of H_2S in the gas phase and significant build-up of sulfur on the carbon on oxidation

Table 1. Surface areas of Saran carbons

Sample	Burn-off (%)	Surface areas ($m^2 g^{-1}$)	
		N_2	CO_2
Unactivated	—	760	880
CO_2 activated	19.6	1160	880
CO_2 activated	38.3	1790	920
CO_2 activated	60.4	2510	820
O_2 activated	18.0	1160	850
Air activated	48.6	1480	720
Air activated	63.8	1250	680

Table 2. Pore volumes of Saran carbons

Sample	Burn-off (%)	Hg	He	Total Open Pore Volume ($cm^3 g^{-1}$)	Macropore Volume ($cm^3 g^{-1}$)
		Density ($g cm^{-3}$)	Density ($g cm^{-3}$)		
Unactivated	—	1.18	2.18	0.388	0.032
CO_2 activated	19.6	0.99	2.18	0.552	0.029
CO_2 activated	38.3	0.79	2.18	0.807	0.066
CO_2 activated	60.4	0.57	2.22	1.305	0.106
O_2 activated	18.0	1.07	2.18	0.477	0.021
Air Activated	48.6	0.88	2.22	0.688	0.038
Air Activated	63.8	0.93	2.22	0.625	0.038

rates. Two runs, each of about five days duration, were conducted consecutively. Between runs, the apparatus was outgassed at 140° and a new charge of gas then admitted. Results of these runs are summarized in Fig. 1, where for convenience the data are only shown for reaction up to about three days. Consider the first run. Over the five day period of reaction the H₂S concentration decreased about 90% and the total sulfur content of the carbon increased to about 18% by weight. As is seen, during the run the instantaneous rate of sulfur build-up on the carbon is directly proportional to the concentration of H₂S in the gas phase. Further, oxidation rates during the second run agree closely with rates during the first run despite further build-up of sulfur on the carbon to about 36% by weight. If oxidation of H₂S is proceeding by the reaction $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{S}_2 + \text{H}_2\text{O}$ it is expected that the rate of the back reaction will be negligible until over 99% of the H₂S is oxidized. That is, at 140° the standard state free energy change for the reaction is highly negative (about -39 kcal/mole). Indeed, the addition of 1% water (7.0 Torr) into the reaction mixture had no detectable effect on oxidation rate.

The long time oxidation runs suggest that H₂S oxidation at 140° is first order with respect to H₂S (or O₂) concentration. By changing the H₂S and O₂ pressure independently, it was found that the reaction is first order in H₂S but zero order in O₂.

The possible reaction of deposited sulfur with O₂ was checked on a carbon sample containing about 10% sulfur. Oxygen (1% by vol.) in He was exposed to the sample at 140° over night with no loss in weight detectable.

The decrease in surface area of the unactivated Saran carbon and the O₂-activated sample with sulfur build-up on the carbons is summarized in Table 3. Significant decreases in area are observed, with the N₂ areas falling off more sharply than the CO₂ areas. Such results are characteristic of molecular sieving. Puri[10] previously suggested controlled addition of sulfur to carbons as a method of producing molecular sieve materials. Taking the density of liquid sulfur at 140° as 1.79 g/cm³[11], it is calculated that the total open pore volumes in the unactivated and O₂-activated samples could hold about 41 and 46% sulfur, by weight, respectively.

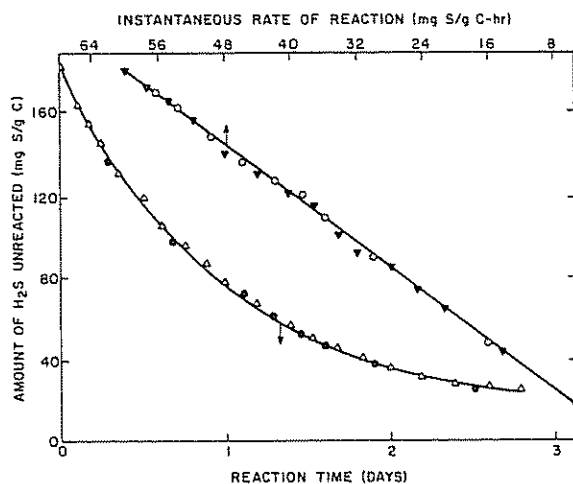


Fig. 1. Long time consecutive runs for the oxidation of H₂S at 140° over O₂-activated Saran carbon. Δ , first run; \circ , second run.

Table 3. Surface area of sulfurized carbons

Sulfur Content (%)	Surface Areas (m ² g ⁻¹)	
	N ₂	CO ₂
Oxygen-activated carbon		
nil	1160	850
10.5	890	620
14.6	730	—
18.5	520	530
30.0	44	160
Unactivated Saran carbon		
nil	770	880
12.1	2	480

3.2.2 Short time oxidation and chemisorption runs

3.2.2.1 Catalytic activity over different carbons. By definition, short time runs are those of about 5 hr duration. Over this period of reaction the decrease in H₂S and O₂ pressure would be less than 10%. Figure 2 shows runs over the unactivated Saran and selected samples activated using different oxidizing gases. During the early stages of reaction, the rate of H₂S oxidation decreases rapidly with increasing reaction time and then becomes essentially constant. Carbons activated in O₂ or air have both a higher initial catalytic activity as well as a higher activity in the "constant-rate" regime than samples activated in CO₂.

3.2.2.2 Rates of adsorption of O₂ and H₂S. It is instructive to compare H₂S oxidation rates with rates of uptake of O₂ and H₂S, separately, on the carbons. Figure 3 shows results for oxygen adsorption. Adsorption is rapid, with oxygen uptake being completed in less than 1 hr. The kinetics of oxygen chemisorption on carbons has been treated in detail by Bansal, Vastola, and Walker[12]. Oxygen uptake is characterized by dissociative

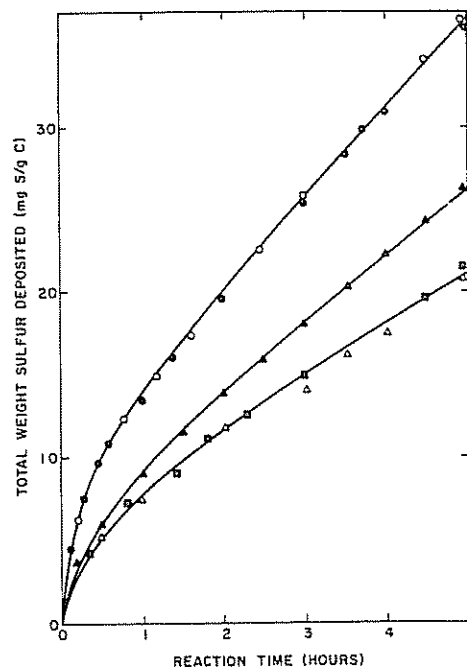


Fig. 2. Runs showing the build-up of sulfur on various carbons as a function of time of oxidation of H₂S at 140°. \square , unactivated and activated in: \circ , O₂ (18% B.O.); \triangle , air (64% B.O.); \blacktriangle , CO₂ (60% B.O.); ∇ , CO₂ (20% B.O.).

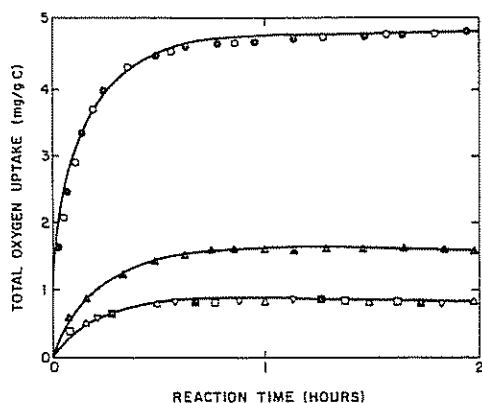


Fig. 3. Runs showing the amount of oxygen uptake on different carbons exposed for various times to an O_2 pressure of 7.6 Torr at 140° . \square , ∇ , unactivated carbon of 150×250 , 65×100 , and 28×48 mesh particle size and carbons activated in: \bullet , O_2 (18% B.O.); \circ , air (64% B.O.); \blacktriangle , CO_2 (60% B.O.); \triangle , CO_2 (20% B.O.).

chemisorption, where the oxygen can only be removed from the surface as CO and CO_2 by outgassing at temperatures considerably in excess of 140° . Since it has been shown that oxygen chemisorption occurs on the prismatic planes (or carbon atoms at the edges of trigonally bonded carbon crystallites), an oxygen atom bonded to a carbon atom would occupy about 8.2 \AA^2 of surface area [13]. On this basis, it is calculated that 1.0 mg of oxygen per g of carbon is equivalent to about $1.5 \text{ m}^2/\text{g}$ of surface. Thus even for the O_2 -activated carbon, results in Fig. 3 show that chemisorbed oxygen would only occupy about $7 \text{ m}^2/\text{g}$ of surface or less than 1% of the total surface of the sample.

The qualitative similarity of rates of H_2S oxidation and oxygen chemisorption shown in Figs. 2 and 3 is striking. That is, the O_2 and air-activated carbons show identical rates for both the oxidation and chemisorption processes. Over the reaction period when the oxidation rate decreases the oxygen chemisorption rate decreases. Over the reaction period where the oxidation rate is essentially constant, oxygen chemisorption is constant and at its maximum value. The rate of oxygen chemisorption and maximum amount chemisorbed on the unactivated Saran carbons and those samples activated in CO_2 are significantly less than for the oxygen-activated samples. This is very suggestive that chemisorption is strongly sensitive to the geometry of the carbon sites on the surface and that activation in O_2 creates a template more susceptible to subsequent oxygen chemisorption than the template created by CO_2 activation. It is also noted in Fig. 3 that the rate of oxygen chemisorption on the unactivated Saran carbon is independent of the particle size used.

In marked contrast to oxygen chemisorption results, it is seen from Fig. 4 that the rate of H_2S adsorption is unaffected by the activation process. Since the three carbons used have very similar CO_2 -surface areas ($850\text{--}882 \text{ m}^2/\text{g}$), these results suggest that H_2S adsorption is primarily nonspecific or physical in nature. Taking the area occupied by a molecule of H_2S as 21.5 \AA^2 [7], the amount of H_2S uptake in 5 hr (about 5 mg/g C) is estimated to result in occupancy of about $19 \text{ m}^2/\text{g}$ (or about 2%) of the surface.

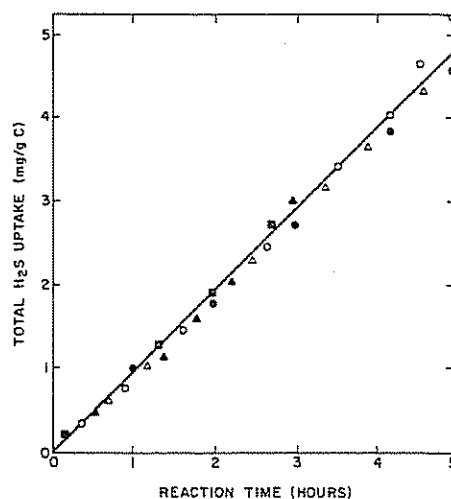


Fig. 4. Runs showing the amount of H_2S uptake on various carbons exposed to an H_2S pressure of 3.8 Torr at 140° . \square , ∇ , \circ , unactivated carbon of 150×250 , 65×150 , and 28×48 mesh particle size and carbons activated in: \bullet , O_2 (18% B.O.); \blacktriangle , CO_2 (60% B.O.).

3.2.2.3 Effect of oxygen pretreatments on catalytic activity. The catalytic activity of the carbon is strongly dependent upon the nature of pretreatment preceding an oxidation run. Generally the carbon was degassed under vacuum at 900° prior to a run. Figure 5 compares the effect of this pretreatment on catalytic activity with pretreatments of (i) outgassing the CO_2 -activated sample at only 140° and (ii) exposing the sample to O_2 at 300° for 30 min. Treatments (i) and (ii) result in decreases of 23 and 54%, respectively, in the steady-state rates as well as decreases in initial rates over the 900° -outgassed sample. Thus the cleaner the surface of the carbon is of oxygen at the beginning of a run the higher its catalytic activity.

Pre-exposure of carbon to H_2 also reduces catalytic activity. For example, activity of the O_2 -activated carbon

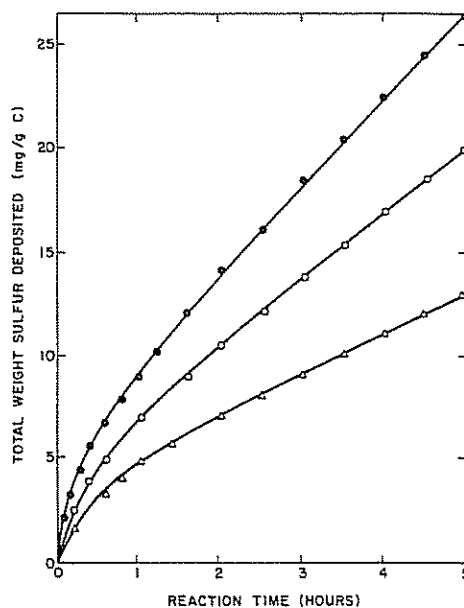


Fig. 5. Runs showing the effect of various pretreatments of the CO_2 -activated carbon (60% B.O.) on its subsequent catalytic activity. \bullet , degassed at 900° ; \circ , degassed at 140° ; \triangle , exposed to 7.6 Torr O_2 at 300° for 30 min.

was reduced about 36% by preexposure to H_2 over night at 140° . The rate curve, however, had the usual shape, that is a more rapid initial rate followed by a region of constant rate. Bansal, Vastola, and Walker have shown that dissociative chemisorption of hydrogen on active carbon sites occurs at 140° [14].

3.2.2.4 Effect of temperature on catalytic activity. Hydrogen sulfide oxidation runs were conducted at temperatures between 100 – 160° over O_2 -activated and unactivated Saran carbons. At temperatures much in excess of 160° , evaporation of sulfur from the carbon becomes significant; and, therefore, a gravimetric technique cannot be used to follow progress of the reaction. Figure 6 presents Arrhenius plots summarizing the results, where rates are

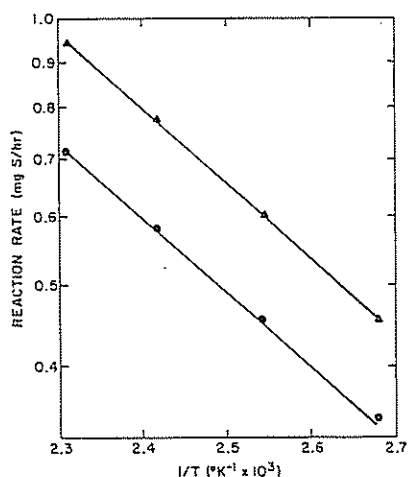


Fig. 6. Arrhenius plots for H_2S oxidation over 125 mg of ● unactivated carbon and ▲ sample activated in O_2 (18% B.O.).

taken in the constant rate regime. The activation energy for the reaction over both carbons is about $4.8 \text{ kcal mole}^{-1}$. As will be discussed later, it appears that the oxidation reaction is proceeding in Zone II. In this case, for a first order reaction the true activation energy for the chemical control step is twice the experimentally-determined activation energy [15]—or $9.6 \text{ kcal mole}^{-1}$ in this case. It is thought noteworthy that a change in slope is not evident in the Arrhenius plots. That is, since monoclinic sulfur melts at about 115° , it might have been thought that the rate of H_2S oxidation would be affected by the physical form (and mobility) of the product sulfur on the surface.

3.2.2.5 Effect of total pressure on H_2S oxidation rate. The effect of the removal of He from the reactant gas mixture and operating at a total pressure of 11.4 Torr (3.8 Torr of H_2S and 7.6 Torr of O_2) was studied at 140° . Over the O_2 -activated carbon, reduction in total pressure resulted in a rate increase from 0.78 to 6.0 mg H_2S oxidized per hr. Such a strong effect is suggestive that the oxidation rate is influenced by mass transport resistance, that is transport of reactants to active sites and products away from active sites. Calculations show that resistance to mass transport

of H_2S in the reactor space above the carbon bed (through the He)* and through the porous bed (height about 0.2 cm) should be negligible [7]. The fact that reduction in carbon particle size from 28×48 mesh (about 0.5 mm) to 150×250 mesh (about 0.08 mm) had no effect on H_2S oxidation rates also might be taken to suggest that mass transport resistance within the carbon particles has a negligible effect on rates. However, the carbon particles do have a distribution of pore sizes, with a significant fraction in voids about 300 Å in diameter, as seen in Table 2. The gas diffusion coefficient in the larger voids would be significantly larger than in the Angstrom-sized micropores in which most of the surface area resides and where the majority of H_2S oxidation is expected to occur. Thus mass transport resistance in the micropores could be significant and yet reduction in particle size would have no effect on H_2S oxidation rate until the particle size was reduced sufficiently to decrease the average length of the micropores. Reduction to only a 150×250 mesh particle size would not be expected to be sufficient to reduce micropore length.

Therefore, assuming that mass transport of reactants and products in the micropores is contributing to controlling the rate of H_2S oxidation or that reaction is occurring in Zone II [15], for a first-order reaction it has been shown that the reaction rate per unit external area of the particles can be expressed as

$$\text{Rate} = C_0 \sqrt{(kAD_{eff})} \quad (1)$$

where C_0 is the reactant concentration outside of the particles, A is the total internal active surface area, and D_{eff} is the effective diffusion coefficient in the pore system in which mass transport is limiting reaction rate.

A reduction in total pressure while keeping the pressure of H_2S and O_2 constant would not change C_0 or k . The possibility that a change in total pressure could affect A is interesting to contemplate. That is, there has been a number of experimental results reported which suggest that a fresh edge carbon site resulting either from carbon gasification or from gas desorption is a nascent site of high activity [16–18]. Further, it is suggested that there are relaxation times associated with the sites decaying to less active sites. The oxidation of H_2S to elemental sulfur and water is highly exothermic (about $54 \text{ kcal mole}^{-1}$). If the mechanism of the reaction is taken to be an H_2S molecule from the gas phase colliding with an oxygen atom chemisorbed on an active carbon site, reaction will result in the removal of the oxygen atom from the carbon site, producing a nascent site. It is suggested that the length of time which the site has excess energy (or excess catalytic activity) decreases with increase in total pressure. That is, each collision of a He atom with a nascent site would be expected to remove some of the excess site energy. Therefore, the average energy of sites undergoing collisions with O_2 would be expected to be decreased. This would, in turn, result in both a decreasing rate of oxygen chemisorption and subsequent H_2S oxidation. At this stage of our knowledge, it is not possible to calculate theoretically the possible change of A with total pressure.

From Figs. 2 and 3 a qualitative relationship between

*The contribution of natural convection to total mass transport in the reaction space, because of the temperature gradient in the vertical reactor tube, is estimated as a major one.

oxidation rates and amounts of oxygen chemisorbed was seen. At saturation coverage the amounts of oxygen picked up were 4.80, 1.60, and 0.85 mg oxygen g^{-1} of carbon on the O_2 -activated, CO_2 -activated, and unactivated carbons, respectively. To a first approximation, if these amounts of oxygen chemisorbed are assumed to be proportional to A in equation (1), taking their square roots and normalizing the data to the unactivated Saran gives values for \sqrt{A} of 2.37, 1.37 and 1.00 for the O_2 -activated, CO_2 -activated, and unactivated samples. From Fig. 2, normalized rates of oxidation over the three carbons are 1.84, 1.32 and 1.00. Thus the square root dependence, rate $\sim \sqrt{A}$, using this crude approach, holds closely when comparing the CO_2 -activated and unactivated samples. Agreement is not as good when comparing the O_2 -activated and unactivated samples.

Change of total pressure in the reactor from 760 to 11.4 Torr might also affect D_{eff} . If D_{eff} were inversely proportional to total pressure the ratio of D_{eff} in the absence and presence of He would be 66.7. Taking the square root of this ratio, according to equation (1), gives a value of 8.1, which is in close agreement with the ratio of oxidation rates in the absence of and presence of He in the reactor, that is 7.7.

In light of the considerations of the possible effects of changes in active area and diffusion coefficients on H_2S oxidation rate, it is surprising that extensive accumulation of sulfur in the pores of the carbon has a negligible retarding effect on reaction rate. The filling of the total pore volume to at least 80% with sulfur apparently results neither in an effective coverage of active sites nor a decrease in D_{eff} . This ability to avoid catalytic deactivation upon extensive sulfur build-up is certainly the key to the possible effective use of porous carbons as catalysts for H_2S oxidation.

3.3 Catalytic activity of commercial active carbons

Hydrogen sulfide oxidation was studied at 140° over three commercial, granular activated carbons. Table 4 presents some pertinent data on the carbons. Each of the carbons has a significant ash content, but the major elements present in the ash are variable. Whereas all the samples have a high SiO_2 content, the Barneby Cheney sample also has a high sodium oxide content; the

Columbian carbon has a high iron oxide content; and the Westvaco carbon, a high aluminum oxide content. The ash contents of the commercial carbons could be reduced substantially by treatment in warm hydrofluoric acid. Ash contents of acid treated Barneby Cheney, Columbian and Westvaco carbons were 0.40, 0.55 and 0.75%, respectively. Nitrogen surface areas were increased less than 10% as a result of acid treatment.

Figure 7 presents results for H_2S oxidation in 5 hr runs over the original and acid treated carbons. By comparison, the oxidation curve for the O_2 -activated Saran carbon (Fig. 2) is almost identical to that of the most active commercial sample, that is the Barneby Cheney carbon. Differences in catalytic activity of the three commercial samples are seen. Acid treatment of the samples had a variable effect on their catalytic activity. That is, activities of the Barneby Cheney and Columbian carbons were reduced; whereas acid treatment had no effect on the catalytic activity of the Westvaco sample. As with the Saran samples, catalytic activity for H_2S oxidation could be correlated with the rate and amount of oxygen chemisorption, as seen in Fig. 8. The fact that acid treatment of the Westvaco carbon had no effect on the

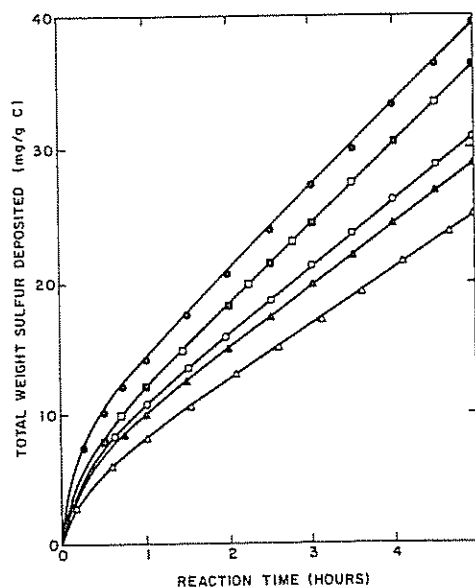


Fig. 7. Runs showing the build-up of sulfur on various commercial carbons as a function of time of oxidation of H_2S at 140° . \odot , Barneby Cheney; \square , Westvaco; \triangle , Columbian. Open circles represent acid-treated samples.

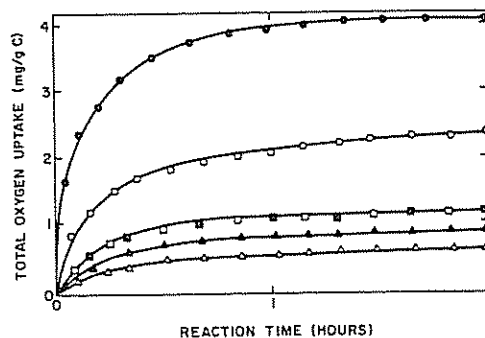


Fig. 8. Runs showing the amount of oxygen uptake on different commercial carbons exposed for various times to an O_2 pressure of 7.6 Torr at 140° . \odot , Barneby Cheney; \square , Westvaco; \triangle , Columbian. Open circles represent acid-treated samples.

Table 4. Analyses of commercial activated carbons

	Barneby-Cheney	Columbian	Westvaco
N_2 surface area ($m^2 g^{-1}$)	1190	1120	1000
Hg density ($g cm^{-3}$)	0.89	0.84	0.92
Ash content (%)	8.25	1.57	5.66
Major constituents of ash (%)			
Al_2O_3	3.1	12.8	32.0
SiO_2	71.2	32.2	41.0
MgO	0.75	1.0	0.85
CaO	2.2	2.2	2.3
Fe_2O_3	3.4	33.6	7.6
Na_2O	11.9	1.2	1.7

rates of H₂S oxidation or oxygen chemisorption clearly shows that it is the composition of the ash which determines whether the ash will have catalytic activity. The two major constituents in the Westvaco ash, silica and alumina, appear to have negligible activity for H₂S oxidation; whereas the sodium oxide in the Barnebey Cheney sample and iron oxide in the Columbian sample appear to have significant activity. That is, the expected removal of sodium and iron by acid treatment appears to be responsible for loss of some catalytic activity in these carbons.

It is noteworthy that the most catalytically active commercial sample, Barnebey Cheney, had a lower rate of oxygen chemisorption and total capacity for oxygen uptake than did the O₂-activated Saran carbon. Normally, commercial carbons are activated in steam-carbon dioxide mixtures. From results on the Saran carbons, it was concluded that activation in CO₂ does not lead to a carbon as active for oxygen chemisorption as one activated in O₂. This perhaps is the reason for the lower activity of the commercial carbons towards O₂ than the activity possessed by the O₂-activated Saran carbon.

The effect of conducting the reaction at a reduced total pressure was also studied over the Westvaco carbon. At a total pressure of 10.6 Torr (consisting of 3.8 Torr of H₂S and 6.8 of O₂), the rate of H₂S oxidation was 9.3 times the rate at 1 atm total pressure. This ratio again compares closely with the square root of the pressure ratio, that is 8.5.

4. CONCLUSIONS

Microporous carbons of high purity have a significant catalytic activity for the oxidation of H₂S to elemental sulfur. The oxidation rate is first order in H₂S pressure and zero-order in O₂ pressure. The rate also varies inversely as the square root of total pressure, where He is used as the diluent. The extent of this catalytic activity can be correlated with the carbon activity for the dissociative chemisorption of oxygen. Thus it is concluded that the reaction involves the interaction of gas phase H₂S with oxygen atoms chemisorbed on carbon active sites. The concentration of carbon sites active to oxygen chemisorption is dependent upon the oxidizing gas used to activate the microporous carbon. That is, the use of O₂ or air as the activating gas media is more

efficient at producing active sites than is the use of CO₂. From activity studies using commercial active carbons of significant ash contents and acid-treated samples in which most of the impurities were removed, it is concluded that some impurities present in some commercial active carbons are also catalysts for H₂S oxidation. } 1?

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REFERENCES

1. Sinha R. K., Ph.D. Thesis, The Pennsylvania State University (1969).
2. Sappok R. J. and Walker P. L. Jr., *J. Air Pollution Control Assoc.* 19, 856 (1969).
3. Lamond T. G., Metcalfe J., III. and Walker P. L. Jr., *Carbon* 3, 59 (1965).
4. Winslow F. H., Baker W. O. and Yager W. A., *Proc. First and Second Carbon Conf.* The Waverly Press, Inc., Buffalo, p. 93 (1956).
5. Brunauer S., Emmett P. H. and Teller E., *J. Amer. Chem. Soc.* 60, 309 (1938).
6. Dubinin M. M., *Chem. Rev.* 60, 236 (1960).
7. Cariaso O. C., Ph.D. Thesis, The Pennsylvania State University (1972).
8. Sinha R. K. and Walker P. L. Jr., *Carbon* 10, 754 (1972).
9. Lamond T. G. and Marsh H., *Carbon* 1, 293 (1963).
10. Puri B. R., *Chemistry and Physics of Carbon*, Vol. 6, p. 191. Marcel Dekker, New York, (1970).
11. Kirk R. E. and Othmer D. F., *Encyclopedia of Chemical Technology*, Vol. 19. Interscience Encyclopedia, Inc., New York (1969).
12. Bansal R. C., Vastola F. J. and Walker P. L. Jr., *J. Colloid Interface Sci.* 32, 187 (1970).
13. Walker P. L. Jr., Austin L. G. and Tietjen J. J., *Chemistry and Physics of Carbon*, Vol. 1, p. 327. Marcel Dekker, New York, (1966).
14. Bansal R. C., Vastola F. J. and Walker P. L. Jr., *Carbon* 9, 185 (1971).
15. Walker P. L. Jr., Rusinko F. Jr. and Austin L. G., *Advances in Catalysis*, Vol. 11, pp. 133-221. Academic Press, New York, (1959).
16. Stacy W. O., Imperial G. R. and Walker P. L. Jr., *Carbon* 4, 343 (1966).
17. Phillips R., Vastola F. J. and Walker P. L. Jr., *Carbon* 8, 197 (1970).
18. Boulanger F., Duval X. and Letort M., *Proc. Third Carbon Conf.*, p. 257. Pergamon Press, New York, (1959).