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INTERACTION OF SULFUR DIOXIDE WITH ACTIVE CARBON

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Abstract—The interaction of SO_2 with a well-outgassed active carbon surface has been studied over the temperature range 50–650°C. SO_2 (0.5 volume %) in He was passed through a packed bed of carbon, the outlet gas stream being monitored by a thermal conductivity cell and a mass spectrometer. Chemisorption of SO_2, and/or its dissociation products, between 50 and 300°C was small, amounting to about 1% of the total surface area. Essentially complete regeneration of the carbon could be achieved by heating at 950°C in flowing He. At 650°C, SO_2 reacted with the carbon rapidly forming CO, CO_2, and elemental sulfur. Significant amounts of the sulfur left the bed and deposited in cooler parts of the reactor. Under these conditions, active carbon is most efficient at removing SO_2.

1. INTRODUCTION

Prevention of the contamination of the atmosphere by SO_2 is one of our most important air pollution problems. One of the possible ways of removing SO_2 from off-gases produced in power and smelter plants is either to adsorb it on active carbon or to react it with O_2 and water over active carbon to produce H_2SO_4 which is adsorbed. In any case, more information is required on the interaction of SO_2 with carbon surfaces.

The sorption of SO_2 on carbon has been studied by several workers who have shown that the presence of oxygen in the system markedly affects the amount of gas adsorbed and the type of adsorption, that is, physical or chemical. Beebe and Dell[1] observed that SO_2 sorption at 0°C on carbon is appreciably enhanced by the presence of surface oxygen and is accompanied by high heats of adsorption at low SO_2 coverage, 12–15 kcal/mole. They concluded, nevertheless, that only physical adsorption occurred. Davtyan and Ovchinnikova[2-5] studied the simultaneous adsorption of SO_2 and O_2 on carbon at 20°C and detected both physical and chemical adsorption; further some SO_2 was oxidized to SO_3. Chemisorption of SO_2 was not found if O_2 was first chemisorbed onto the carbon and SO_2 subsequently adsorbed in the absence of gaseous O_2. Billinge[6] investigated the adsorption of SO_2 at 70 and 100°C in a flow system using a simulated flue gas. The presence of O_2 resulted in surface oxidation of the SO_2 to SO_3 and also somewhat increased the sorption capacity of the carbon. However, as previously noted by Davtyan and Ovchinnikova[3,4] the greatest enhancement of SO_2 sorption occurred in the presence of O_2 and water vapor.

For the chemisorption of SO_2 at room temperature, Davtyan and Ovchinnikova[2,3] concluded that this only involves surface oxides very weakly bonded to the carbon surface and in equilibrium with gaseous O_2. They could be quickly removed by evacuation at 20°C. However, at higher temperatures it might be expected that chemisorption proceeds somewhat differently. Thus, we have examined SO_2 interaction with carbon between 50 and 650°C, initially in the absence of O_2 or any other gas, to study the effect of interaction temperature on carbon capacity and the subsequent ease of carbon regeneration at higher temperatures.

2. EXPERIMENTAL

This study was made in a flow system using a medium activated coconut shell charcoal: 4×10 mesh particle size, 1100 m^2/g surface area, 0.6 g/cm^3 apparent density and 1.6% ash. The carbon, 13–14 g, was packed in a bed 8–9 cm high and approximately 2.5 cm diameter. The bed was contained in a column which could be attached to a vacuum line for baking and outgassing and then transferred to the flow system without exposing the charcoal to the atmosphere. A small tube furnace surrounded the column and maintained the bed at the desired temperature during a sorption experiment. Gas flow through the bed was 200 cm^3/min (NTP). With a bed porosity of ca 31%, the effective linear flow was 153 cm/min. The average residence time in the bed was 3.5 sec. The gas stream flowing into the bed was 0.5% SO_2 in He (equivalent to 4.5×10^{-5} g moles of SO_2/min). Removal of SO_2 from the stream was monitored by a thermal conductivity cell coupled to a recorder. The feed and exit gases were sampled for subsequent analysis by mass spectrometry. Each sorption experiment was continued until the SO_2 concentration in the effluent gas equalled that in the feed stream. SO_2 retained by the bed was determined by weighing. Physically adsorbed SO_2 was removed by evacuation at the sorption temperature or, if necessary, by purging with He at 200°C. A value was then obtained for chemisorbed SO_2.*

All the sorption experiments to be discussed were carried out on the same initial sample, except for the runs at 600 and 650°C. For the first experiment the bed was prepared by outgassing to a pressure of 10^{-5} torr at 950°C. Subsequent experiments were made after the charcoal had been regenerated in flowing He (200 cm^3/min at 760 torr pressure) at 950°C or any other desired temperature. A typical regeneration time at 950°C was 90 min.

*It is important to appreciate that when we refer to chemisorbed SO_2 throughout the paper we are not necessarily implying that the undissociated SO_2 molecule has chemisorbed on the carbon. To a greater or less extent, dependent upon the interaction conditions, SO_2 may be dissociating at the carbon surface and its products chemisorbing.

3. RESULTS

Initially, several sorption experiments were carried out at 150°C to determine how completely the capacity of the bed could be restored following heat treatment in He at 950°C. These results are summarized in Table 1. Regeneration of the charcoal activity was essentially complete. Runs were then made at temperatures between 50 and 300°C. The charcoal was regenerated at 950°C following each adsorption run, unless otherwise indicated. Results of these experiments are also summarized in Table 1. The main points to be noted are:

(1) An oxygen-free carbon surface has limited total SO_2 sorption capacity. Further, chemisorbed SO_2 occupies an area of, roughly, only 1% of the BET area, assuming that one SO_2 molecule occupies one carbon site in the prismatic plane of a graphite-like crystallite.

(2) Between 50 and 300°C, the amount of SO_2 chemisorbed is not appreciably affected by temperature.

(3) Physical adsorption decreases sharply with increasing temperature between 50 and 150°C from 3% to 0.3%. Above 250°C, physical adsorption is negligible.

Typical weight losses accompanying the regeneration of the charcoal after SO_2 chemisorption are shown in Table 2. Samples were held at each temperature until the desorption of gaseous products was insignificant. Weight losses occurred mainly above 600°C. Over the entire temperature range, the only gases evolved were oxides of carbon. Trace amounts began appearing at about 300°C. Whether CO or CO_2 appeared first seemed to depend upon the amount of sulfur present on the carbon, as will be discussed later. Between 600 and 700°C CO and CO_2 were present in significant amounts, but at 800°C CO_2 had practically disappeared.

TABLE 1. VARIATION OF SO_2 SORPTION WITH TEMPERATURE AND REGENERATIVE WEIGHT LOSS

Experiment No.	Sorption temperature and details of charcoal preparation	Sorption-wt% of outgassed carbon Total %	Chem. %	Phys. %	% Wt loss regeneration at 950° C
1A	SO_2 sorption at 150° C on charcoal outgassed at 950° C	1.24	1·04	0.20	0.78
2A	SO_2 sorption at 150° C on 1A charcoal after regeneration at 950° C	1.11	0·83	0.28	1.14
3A	SO_2 sorption at 150° C on 2A charcoal after regeneration at 950° C	1.18	0·82	0.36	0.81
5A	SO_2 sorption at 150° C on 3A charcoal after regeneration at 950° C	1.08	0·82	0.26	0.33*
6A	SO_2 sorption at 150° C on 5A charcoal after regeneration at 650° C	0.93	0·72	0.21	0.15†
7A	SO_2 sorption at 150° C on 6A charcoal after regeneration at 500° C	0.36	0·29	0.1	1.08
8A	SO_2 sorption at 300° C on 7A charcoal after regeneration at 950° C	1.08	1·08	nil	0.85
9A	SO_2 sorption at 250° C on 8A charcoal after regeneration at 950° C	1.05	1·05	nil	0.94
10A	SO_2 sorption at 100° C on 9A charcoal after regeneration at 950° C	1.78	0·99	0.79	0.86
11A	SO_2 sorption at 50° C on 10A charcoal after regeneration at 950° C	4.13	0·93	3.20	—

* Regeneration at 650° C.
† Regeneration at 500° C.

Sulfur compounds were not detected at any temperature. It is interesting to compare this regeneration behavior with that where SO_2 sorption has occurred from a simulated flue gas, containing water and O_2. In this case, the SO_2 was almost completely recovered as such in the range 300 to 400°C.[6]

Additional regeneration experiments (summarized in Table 1) indicated that roughly 80% of the initial sorption capacity of the charcoal was restored by heat treatment (HT) at 650°C. With a further decrease in HT temperature, restoration efficiency fell off rapidly; that is, at 500°C only 30% restoration was effected. In a

TABLE 2. REGENERATION OF CHARCOAL SATURATED WITH CHEMISORBED SO_2 AT 150° C

Regeneration Temp. (°C)	Cumulative Wt. Loss, %
300	0.00
400	0.00
500	0.12
600	0.30
700	0.40
800	0.52
900	0.73
950	0.81

TABLE 3. SULFUR CONTENT OF CHARCOAL FOLLOWING SORPTION AND REGENERATION AT VARIOUS TEMPERATURES

Sample history	Regeneration		Sulfur content (%)
	Time (min)	Temperature (°C)	
SO_2 sorption at 150° C	—	—	0.68
Regeneration	90	400	0.62
Regeneration	90	600	0.56
10 hr of continuous and complete SO_2 removal at 650° C from the gas stream	—	—	3.80
Outgassed at 950° C followed by SO_2 sorption at 300, 400, and 450° C. After each sorption the sample was regenerated at 950° C for 90 min and after the final regeneration the sulfur content of the charcoal was determined	90	950	2.03

subsequent SO_2 sorption experiment at 650°C, uptake of SO_2 was continuous (complete removal from the He stream for at least 7 hr was found). Concurrently, the appearance of elemental sulfur on the cooler parts of the column was noted. From these observations, it was concluded that regeneration of the charcoal after SO_2 saturation at lower temperatures, 50–300°C, was essentially through the reduction of chemisorbed SO_2 to elemental sulfur, which condensed on the column and escaped detection. However, analysis showed that the regenerated charcoal still contained significant sulfur. Listed in Table 3 are the sulfur contents of three charcoal samples following SO_2 sorption and regeneration as described. From the results, it is obvious that initial restoration of the sorption capacity after SO_2 saturation at 50–450°C

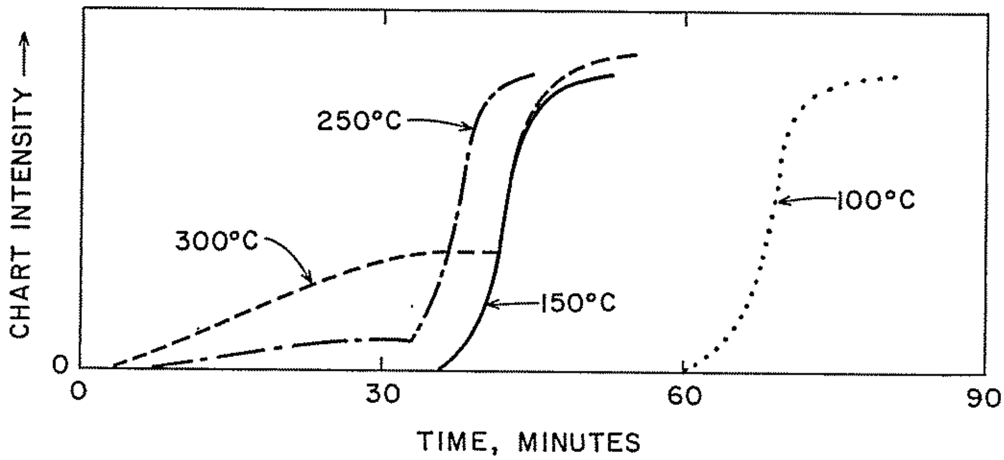

FIG. 1. Recorder trace of breakthrough curves for SO_2 removal on medium activated coconut shell charcoal between 100 and 300°C.

cannot be attributed to sulfur release from the carbon but is due to either (a) surface migration of sulfur from the original adsorption sites or (b) the creation of new sites as a result of CO and CO_2 evolution.

Although the amount of SO_2 chemisorption between 50 and 300°C is temperature independent, at 250 and 300°C slight chemical reaction was observed. In Fig. 1 recorder traces are reproduced of the breakthrough curves at different temperatures. At 100 and 150°C the trace intensity remained on zero, until breakthrough some 40 to 60 min later, indicating complete removal of SO_2 and the absence of any gaseous reaction products during this period. Following breakthrough, the trace intensity quickly increased to a value equivalent to that produced by the inlet concentration of SO_2. At 250 and 300°C, a different type of trace was obtained. Shortly after the start of the runs the trace intensity increased gradually for ca 33 min and 42 min at 250 and 300°C, respectively. Analysis of the exit gases during this period showed the complete absence of SO_2 and, instead, the presence of CO. For example, at 300°C about 1.8×10^{-3} g moles of SO_2 were held up by the active carbon during this period and 0.32×10^{-3} g moles of CO appeared in the exit gas. At the end of this period, breakthrough of SO_2 commenced at both 250 and 300°C. At 250°C, CO evolution ceased following saturation of the bed with SO_2. However, at 300°C, for the run shown, some SO_2 was still being removed by the bed at the end of the run and CO evolution was continuing.

At higher temperatures, 600 and 650°C, CO and CO_2 were almost immediately observed in the exit gas, CO_2 being the major constituent. At 600°C, breakthrough of SO_2 occurred after ca 2.5 hr. At 650°C, breakthrough did not occur during the duration of the experiment, namely 7 hr; and at the end of this time, elemental sulfur had freely accumulated on the cooler surfaces of the adsorption column. Upon removing and weighing the charcoal, it is estimated that roughly 40% of the total sulfur deposited on the cooler surfaces; the remainder was held in the charcoal.

4. DISCUSSION

As found previously,[2-6] the capacity of active carbon to retain SO_2 in the absence of oxygen and water is small. It is uncertain whether SO_2 chemisorption at temperatures up to 150°C is dissociative or not. Certainly, however, the appearance of significant amounts of CO in the exit gas at 250 and 300°C indicates that chemisorption is now at least partly dissociative. LEPSOE [7] concludes that the reduction of SO_2 by carbon is expressed satisfactorily by the consecutive reactions

$$SO_2 + C = CO_2 + 1/2\ S_2 \qquad (1)$$

$$CO_2 + C = 2\ CO \qquad (2)$$

The appearance of CO as a product at 250–300°C (and, in fact, up to about 700°C) cannot be attributed to this reaction sequence, however, since the rate of reaction (2) will be insignificant at these temperatures.[8] Rather it is suggested that an oxygen-transfer reaction takes place between SO_2 and carbon, analogous to the well-known reaction in the case of CO_2 and carbon.[8] An intermediate reactive oxygen complex is formed, which can either desorb as an oxide of carbon or convert to a more stable oxygen complex.[9] Curiously, at 300°C the only oxide of carbon recovered is CO; CO_2 is recovered along with CO only at 600–650°C. This is in direct contrast to the CO/CO_2 product ratio in the C–O_2 reaction, where the ratio increases in value with increasing temperature.[10]

We have shown previously that both CO and CO_2 are formed from atomic intermediates in the C–O_2 reaction [11] and suggest that they are derived from oxygen complexes in carbonyl and lactone structures, respectively. SMITH and co-workers[12] have shown, using infrared absorption, that these structures are formed when carbon is exposed to oxygen at room temperature but that upon heating to higher temperatures in vacuo, more CO_2 is produced first and the concentration of the lactone structure decreases more rapidly than the carbonyl structure. In the present studies, when the charcoal was regenerated following adsorption of SO_2 at 150°C (run 2A, see Table 1), CO_2 did appear first and then CO appeared at about 800°C. However, during regeneration following adsorption of SO_2 at 150° in subsequent runs (runs 3A and 5A), CO appeared first and CO_2 did not appear until about 500°C. It is known that the sulfur content of the active carbon increased as the number of regenerations increased. Thus, one is tempted to suggest that the presence of sulfur on the carbon surface is either affecting the relative availability of peripheral carbon sites which can form carbonyl and/or lactone structures or the relative thermal stability of these complexes once they are formed. The fact that only CO is evolved above 800°C during regeneration we attribute to the significant rate of reaction (2).

LEPSOE,[7] among others, suggested that CO_2 can also be produced by the reaction

$$SO_2 + 2\ CO = 2\ CO_2 + 1/2\ S_2 \qquad (3)$$

TABLE 4. MATERIAL BALANCES ON REACTION SYSTEMS SO_2–C AND SO_2–CO–C

	Gaseous reactants, moles $\times 10^{-5}$/min		Time product sample taken	Gaseous products, moles $\times 10^{-5}$/min			
Temp. (°C)	SO_2	CO	Min	SO_2	CO	CO_2	COS
650	4.5	nil	420	nil	1.0	3.8	nil
600	4.5	nil	130	nil	0.5	1.8	nil
550	4.5	17.0	15	0.4	8.9	8.6	0.2
550	4.5	17.0	195	0.4	8.2	7.7	0.4
500	4.5	17.0	240	nil	6.6	10.6	1.2
350	4.5	17.0	330	nil	4.6	9.6	3.4

We studied this reaction briefly over our charcoal bed at 550, 500, and 350°C. A mixture of SO_2 (0.5%) and CO (2%) in He was passed through the bed at 200 cm³/min commencing at 550°C. After 195 min the temperature was lowered to 500°C; after an additional 45 min it was lowered to 350°C. The experiment was finally discontinued following an additional 45 min at 350°C. Comparison of the results obtained on the two systems, that is, SO_2–C and SO_2–CO–C (Table 4), shows that the presence of CO considerably modified the mechanism by which sulfur was produced. The major results can be summarized as follows:

(1) The mass balance for the system SO_2–CO–C indicates no net loss of carbon from the bed.

(2) For the system SO_2–C at 600°C after more than 2 hr (when SO_2 still had not broken through the bed) more than 50% of the oxygen associated with the SO_2 was still being retained by the bed. However, at 550°C in the system SO_2–CO–C, with the same bed weight and SO_2 flow rate, essentially no oxygen was being retained by the bed. Apparently, CO completely inhibited oxygen complex formation on the carbon surface.

(3) At 550°C, the ratio of CO/SO_2 reacting was ca 2. This suggests that reaction (3) was taking place. However, when the temperature was decreased to 350°C, the ratio of CO to SO_2 reacting increased to 2.8; and 75% of the sulfur from the SO_2 that was reacting was found in the product COS. This suggests that CO was reacting with a sulfur–oxygen surface complex.

In conclusion, it is obvious that low temperature chemisorption of SO_2 on active carbon (in the absence of O_2 and water) is an impractical method of retention. One possibility for its removal is to operate at temperatures sufficiently high for SO_2 to not only dissociate at the carbon surface but also for most of the products formed, that is sulfur and oxygen complexes, to either leave the carbon bed or at least migrate to less active sites. In this manner, active sites will continue to be produced and be available for further reaction with SO_2.

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