

THE MECHANISM OF SO₂ REMOVAL BY CARBON

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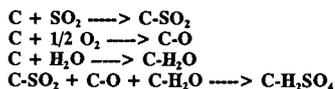
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INTRODUCTION

There are a number of research groups currently involved in the development of novel carbon-based processes and materials for removal of SO₂ from coal combustion flue gas [1-16]. The type of carbon used more often than not dictates the economic viability of a given process. A high quality carbon adsorbent for SO₂ removal should have a high adsorption capacity, rapid adsorption kinetics, low reactivity with oxygen, minimal loss of activity after regeneration, low pressure drop, high mechanical strength, and low cost. The objective of this study [17-23] has been to produce activated char from Illinois coal with optimal SO₂ removal properties, and to gain a better understanding of SO₂ removal by carbon.

The reaction of SO₂ with carbon in the presence of O₂ and H₂O at relatively low temperatures (80-150°C) involves a series of reactions that leads to the formation of sulfuric acid as the final product. The overall reaction is $SO_2 + 1/2 O_2 + H_2O + C \rightarrow C-H_2SO_4$. Most studies that have sought to maximize the SO₂ removal capabilities of a carbon only assume a certain mechanism for SO₂ adsorption and conversion to H₂SO₄ is operable. In the literature [1-5,8,10,24], the following reaction sequence has usually been presented before beginning any discussion on SO₂ removal by carbon.



It implies that SO₂, O₂ and H₂O are all adsorbed on the surface of the carbon in close enough proximity and in the proper steric configuration to react and form H₂SO₄. A clearer understanding of this sequence of reactions will no doubt lead to the development of activated carbons better suited for adsorption of SO₂ and its conversion to H₂SO₄. In this paper, we examine the effect of surface area and chemisorbed oxygen on the SO₂ adsorption capabilities of chars prepared from a bituminous coal. Using temperature programmed desorption, we titrate the carbon sites responsible for adsorption of SO₂ and its conversion to H₂SO₄, and based on the experimental results, we propose a more detailed mechanism for SO₂ removal by carbon.

EXPERIMENTAL

Activated chars were prepared from a sample of Illinois Colchester (No. 2) hvC bituminous coal (IBC-102) obtained from the Illinois Basin Coal Sample Program. A 2 in. ID batch, fluidized-bed reactor was used to pyrolyze 200 g of 48x100 mesh coal (N₂, 900°C, 0.5 h) and activate the resultant char (H₂O, 860°C, 30% conversion). The steam activated char was treated with nitric acid (10 M HNO₃, 80°C, 2 h) to modify its pore structure and surface chemistry. The HNO₃-treated char was heated in nitrogen to various temperatures (200-925°C) and held there for 1 h to desorb carbon-oxygen (C-O) complexes formed during the HNO₃ treatment. A commercial activated carbon (Calgon F400) was also studied. SO₂ adsorption capacities of prepared carbons were determined by thermogravimetric analysis using a simulated flue gas containing 2500 ppm SO₂, 5% O₂, and 7% H₂O. Temperature programmed desorption (TPD) experiments (N₂, 25-1000°C, 5°C/min, 1 h at 1000°C) were performed to determine the amount of oxygen adsorbed on the char surface. Further details of the experimental equipment and procedures used in this study are provided elsewhere [19-21].

RESULTS AND DISCUSSION

Table 1 shows how poor the correlation is when SO₂ adsorption capacities of chars are normalized with respect to their surface areas or oxygen contents. It is interesting to note that the steam activated IBC-102 char (H₂O, 860°C) and untreated Calgon F400 carbon have comparable SO₂ adsorption capacities despite a large difference in N₂ BET (77 K) surface area; their CO₂ BET (195 K) surface areas seem to correlate better with SO₂ adsorption capacity. Table 1 also shows that the SO₂ adsorption capacity of the nitric acid treated, thermally desorbed chars increases with increasing thermal desorption temperature. A similar effect of heat treatment (at 800°C) on the SO₂ adsorption capacity of polyacrylonitrile-based activated carbon fibers was recently reported by Mochida and his research group [7,11,12], and attributed to an increase in the number of active sites generated by the evolution of CO and CO₂ during decomposition of C-O functional groups. Davini [25,26] ascribed enhanced SO₂ adsorption on oxidized activated carbon to the presence of basic C-O groups on the carbon surface. Most recently, Kim et al. [13] and Fei et al. [14] proposed that the inherent nitrogen in polyacrylonitrile and shale oil derived activated carbon fibers, respectively, increases their catalytic activity for SO₂ adsorption and conversion to H₂SO₄.

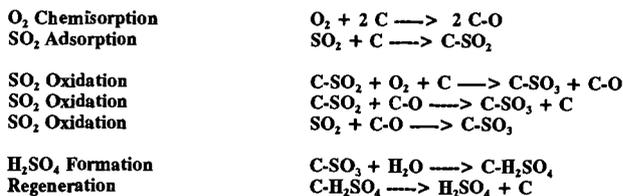
The TPD profiles of thermally desorbed, nitric acid treated IBC-102 chars shown in Figure 1 indicate

that the absence of oxygen on the carbon surface results in a char with highest SO₂ adsorption capacity (e.g., HNO₃-925°C char). Apparently, carbon atoms, which are not tied up by an adsorbed oxygen atom, have valence electrons that are more available, and are more reactive towards SO₂ adsorption. We, therefore, postulate that the unoccupied or free sites control the uptake of SO₂. It is well known that once carbon is evolved as CO or CO₂ during carbon gasification, a new carbon atom of equal or greater reactivity will be exposed. These newly exposed carbon atoms, coined nascent sites by Phillips et al. [27], in many cases define the surface chemistry of a carbon [28,29]. It is these nascent sites, made active by the thermal desorption treatment at 925°C, that we believe are responsible for enhanced SO₂ adsorption on the HNO₃-925°C char. Nitric acid, being a very strong oxidant, oxidizes the surface of the carbon so that even carbon atoms that would otherwise not react with the oxygen in air are oxidized. Upon thermal desorption treatment, a once relatively unreactive carbon atom is released as CO or CO₂, leaving behind a carbon atom which is then primed to react with SO₂. The evolution of CO or CO₂ also serves to activate the pore structure thereby widening the pores making them more accessible to reactant gases; this could also increase SO₂ adsorption. A parallel study with activated carbon fibers (ACF) in our laboratory [30], however, has shown that ACF with smaller pores (9 Å) and lower surface areas (600 m²/g) actually adsorb more SO₂ than higher surface area ACF (1900 m²/g) having larger pores (18 Å). This increase in SO₂ adsorption for low surface area fibers is presumably due to enhanced adsorbent-adsorbate interactions caused by the smaller average pore size [31].

To test our hypothesis that free sites are primarily responsible for SO₂ adsorption, the TPD profiles of the nitric acid treated, thermally desorbed IBC-102 chars of Figure 1 were utilized. We defined the free sites for this series of chars as being those sites that were once occupied by oxygen because of nitric acid treatment, but now, because of the thermal desorption treatment, had become unoccupied or free. To quantify the CO free sites for a given char, say, the HNO₃-725°C char, we subtracted its CO evolution profile from the one of the original nitric acid treated char (Figure 2). The unshaded region in Figure 2 represents the number of free sites that are created by CO evolution during the thermal desorption treatment at 725°C. Table 2 lists the number of both the CO and CO₂ free sites calculated for each of the nitric acid thermally desorbed IBC-102 chars. The last two columns show the SO₂ adsorption capacities normalized with respect to the CO and CO₂ free sites. The SO₂ adsorption capacity is seen to vary by a factor of 1.6 and 2.8 when normalized with respect to CO and CO₂ free sites, respectively. This is an excellent correlation compared to those we found for surface area or adsorbed oxygen (Table 1). To the best of our knowledge, this type of quantitative approach has never before been used to explain SO₂ removal by carbon. The concept of free or unoccupied sites was first postulated and utilized by Laine et al. [32] to explain the gasification reactivity of carbon in oxygen. Our new approach for analyzing TPD data shows that it may be possible to titrate directly the free sites responsible for SO₂ adsorption and conversion to H₂SO₄. A slight variation in this same approach could be used to explain results in other studies that have examined SO₂ removal by carbon. For example, Davini [25,26] found that the SO₂ adsorption capacity of a commercial grade carbon increased with an increase in activation temperature. The activation conditions he used ranged from 300°C in air to 800°C in 2% O₂. Char gasification reactivity studies have shown that less oxygen will adsorb on the carbon surface at higher temperatures and in lower pressures of an oxidizing gas [28,33,34]. The higher temperature used by Davini during activation is likely to have deposited less oxygen on the carbon surface, thus preserving more free sites for reaction with SO₂. In fact, further analysis of his SO₂ and O₂ adsorption data [26] using our concept of free sites shows that the SO₂ adsorption capacities of two groups of carbons that each varied by more than a factor of three, could be made to vary by less than a factor of 1.2 when normalized to the total number of free sites.

This procedure for assessing free adsorption sites was also applied to the Calgon F400 carbon (also a steam activated bituminous coal char). Table 2 shows that there was no significant improvement in the SO₂ capacity of this carbon with our nitric acid, thermal desorption treatment, perhaps because its pore structure was already optimized for adsorption of contaminants. Table 2 shows that the SO₂ adsorption capacity of the Calgon F400 carbons normalized with respect to the number of CO and CO₂ free sites also varies by less than a factor of 2 and 3, respectively. It is interesting to note the almost one to one ratio of SO₂ adsorption capacity to CO free sites for both the IBC-102 and Calgon F400 carbons.

Based on these experimental results, we propose the following sequence of reactions to explain the mechanism of SO₂ removal by carbon.



Adsorption of SO₂ and O₂ occurs in parallel on the free carbon active sites (denoted by C). Molecular oxygen dissociates on two free sites to form a pair of C-O complexes. SO₂ competes with O₂ for free sites. The reaction of oxygen with carbon produces a stable C-O complex, which apparently inhibits

SO₂ adsorption. The next step is the oxidation of SO₂ to SO₃. Conceivably, three reactions are possible. The C-SO₂ complex can react directly with molecular oxygen in the vicinity of a free site to form a C-SO₃ intermediate and stable C-O complex. SO₂ oxidation could also be accomplished by the reaction of either the C-SO₂ complex or SO₂ with the C-O complex. However, the occurrence of these two reactions is less likely since we observed an inverse correlation between SO₂ adsorption and stable C-O complex. The conversion of stable C-O complex into a reactive C(O) intermediate, as proposed in recent carbon gasification studies [33-36], may also influence SO₂ adsorption and conversion to H₂SO₄ [19].

According to the SO₂ removal mechanism often presented in the literature (see Introduction), one could assume that the more oxygen adsorbed on the carbon surface, the more SO₂ will be adsorbed. In this study, we have seen that the formation of stable C-O complex during char preparation serves only to occupy otherwise reactive free adsorption sites, and that the C-O complex probably is not an essential reaction intermediate in the conversion of SO₂ to H₂SO₄. It may also be that our TPD method did not titrate those C-O complexes responsible for catalytic oxidation of SO₂ to SO₃, and that a fleeting C(O) complex, formed contemporaneously with SO₂ adsorption and/or by transformation of stable complex into reactive intermediate, acts as the "catalyst." Isotope labelling studies could be useful in determining if such an intermediate exists [37]. Another question is whether SO₂ removal would occur if there was no oxygen in the flue gas and/or adsorbed on the carbon surface. This was resolved by using two of the IBC-102 chars, one with some adsorbed oxygen (HNO₃-525°C) and one with essentially no adsorbed oxygen (HNO₃-925°C). Figure 3 shows that, with 5% O₂ in the flue gas, the HNO₃-925°C char adsorbs the most SO₂. With no oxygen in the flue gas, this char still adsorbs SO₂, but in this case, it is not converting C-SO₂ to H₂SO₄ due to a lack of oxygen. SO₂ adsorption is enhanced for both chars when oxygen is present in the flue gas (compare 0 and 5% O₂ plots in Figure 3). The adsorption of SO₂ on a free site is seen to account for nearly 50% of the weight gain for both chars. This data seems to support the first SO₂ oxidation mechanism, i.e., the one involving the reaction of adsorbed SO₂ with O₂ and a free site to form C-SO₃.

Hartman and Conghlin [38] found the catalytic oxidation of SO₂ to SO₃ by carbon to be the rate determining step in the overall reaction. If the rate determining step is, indeed, catalytic oxidation of SO₂ to SO₃, and assuming that the first SO₂ oxidation reaction is operable, the overall rate of reaction could be expressed as

$$\text{rate} = k_2 [C] [C-SO_2] [O_2]$$

where k_2 is a fundamental rate constant. The unknowns in this expression are k_2 and the concentration of C-SO₂ complex. At steady state, the rates of each of the reactions in the mechanism presented above are equal to that of the rate determining step, and by definition, the concentration of each of the intermediate species does not change with time. Thus,

$$\frac{d[C-SO_2]}{dt} = 0 = k_1 [C] [SO_2] - k_2 [C] [C-SO_2] [O_2]$$

Solving for [C-SO₂],

$$[C-SO_2] = \frac{k_1 [C] [SO_2]}{k_2 [C] [O_2]} = \frac{k_1 [SO_2]}{k_2 [O_2]}$$

and substituting this into the rate expression,

$$\text{rate} = k_1 [C] [SO_2]^n$$

where n is the order of reaction with respect to SO₂. The rate is then only a function of the concentration of free sites and the partial pressure of SO₂, a departure from the more elaborate rate expressions recently proposed by others (see, for example, refs. [2] and [24]). For concentrations of SO₂ less than 1500 ppm, we found values of n between 0.5 and 1, and for concentrations of SO₂ greater than 1500 ppm, the value of n approached zero (Figure 4). Nevertheless, at a constant partial pressure of SO₂, the rate of SO₂ adsorption and conversion to H₂SO₄ should be directly proportional to the number of free adsorption sites as confirmed by our TPD experiments. It remains to be determined whether this TPD method can be applied to adsorption of other contaminants in flue gas. If so, it could facilitate preparation of activated char optimized for removal of SO₂ as well as other air toxics (e.g., nitrogen oxides, mercury) from combustion flue gas. Recent studies suggest that adsorption of NO_x and reduction to N₂ is more or less controlled by free sites on the carbon surface [39-41].

In the above mechanism, the C-SO₃ intermediate reacts with water to form sulfuric acid. The free site returns to its original state after regeneration. The water adsorbed in the pores may act as a regeneration medium. The acid adsorbed on the carbon surface will be continuously removed by a reservoir of water adsorbed in the pores. As the acid goes into solution, the free site once again becomes reactive towards SO₂ adsorption. Thus, the site can undergo numerous cycles of adsorption/desorption without any external means of regeneration. The production of H₂SO₄ proceeds indefinitely until water adsorbed in the pores becomes saturated with H₂SO₄ and/or the free sites

become occupied with oxygen, at which point the spent carbon needs to be regenerated, e.g., thermal treatment or flushing with water or dilute acid. (The latter treatment will not remove any of the C-O complex). Thus, it can be expected that the amount of water retained in the pore volume of the carbon should determine its equilibrium SO₂ adsorption capacity, which may require more than 40 h to attain (Figure 4); whereas, the rate (or kinetics) of SO₂ adsorption, say, in the first 6 h of adsorption, will be controlled by the number of free sites. In an earlier paper, Jungten and Kuhl [3] hypothesized that the active sites would control the rate of SO₂ adsorption, but this was never verified experimentally. The observed increase in the SO₂ adsorption capacity of nitric acid treated chars with increasing thermal desorption temperature is probably due to both an increase in the concentration of free active sites and in the accessible pore volume of the char. The latter leads to a greater reservoir for storage of dissolved H₂SO₄ and an increased ability to regenerate the active sites for additional SO₂ adsorption.

CONCLUSIONS

In this study, we found the SO₂ adsorption capacity of a coal char to be inversely proportional to the amount of oxygen adsorbed on its surface. Temperature programmed desorption was used to titrate those sites responsible for adsorption of SO₂ and conversion to H₂SO₄. Based on these results, a detailed mechanism for SO₂ removal by carbon was proposed. The derived rate expression shows SO₂ adsorption to be dependent only on a fundamental rate constant and concentration of carbon atoms we designate as free sites. The results obtained here are analogous to those of a recent study [33] which found that a similar relationship exists between the specific rate (R_{sp}) of carbon gasification in carbon dioxide and the number of reactive sites measured initially by transient kinetics (TK) experiments and later confirmed by TPD, i.e., R_{sp} = k [C]. In that study, TK and TPD were used to titrate those occupied sites or C(O) intermediates responsible for controlling the rate determining desorption step in CO₂ gasification of carbon. The results of both studies seem to support a unified approach to the reactions between carbon and oxygen-containing gases, as most recently proposed by Chen [42] and Moulijn and Kapteijn [43].

ACKNOWLEDGEMENTS

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Table 1. Correlation of SO₂ adsorption capacity with surface area and adsorbed oxygen.

Sample	SO ₂ Capacity ¹ (mg SO ₂ /g char)	N ₂ BET (m ² /g)	CO ₂ BET (m ² /g)	SO ₂ /N ₂ (mg/m ²)	SO ₂ /CO ₂ (mg/m ²)	O ₂ (wt%)	SO ₂ /O ₂
IBC-102, 900°C, 0.5 h	7	1.2	98	5.8	0.07	0.5	1.40
IBC-102, 900°C; H ₂ O, 860°C	176	220	613	0.80	0.29	1.1	16.0
IBC-102, 900°C; H ₂ O, 860°C; HNO ₃	---	400	585	0.06	0.04	16.4	---
IBC-102, 900°C; H ₂ O, 860°C; HNO ₃ , 525°C	91	460	693	0.20	0.13	5.9	1.54
IBC-102, 900°C; H ₂ O, 860°C; HNO ₃ , 725°C	241	500	727	0.48	0.33	1.6	15.0
IBC-102, 900°C; H ₂ O, 860°C; HNO ₃ , 925°C	287	550	726	0.05	0.39	0.5	57.4
Calgon F400	206	1000	1000	0.21	0.21	0.5	41.2
Calgon F400, HNO ₃	---	---	---	---	---	15.7	---
Calgon F400, HNO ₃ , 200°C	46	600	---	0.08	---	14.3	0.32
Calgon F400, HNO ₃ , 525°C	117	456	---	0.26	---	5.6	2.09
Calgon F400, HNO ₃ , 725°C	156	533	---	0.29	---	3.4	4.59
Calgon F400, HNO ₃ , 925°C	214	463	---	0.46	---	1.7	12.6

¹ SO₂ capacity determined after 6 h.

² not determined.

Table 2. Correlation of SO₂ adsorption capacity with free adsorption sites.

Sample	SO ₂ capacity ¹	Adsorbed oxygen ¹	CO/CO ₂	CO free sites ^{1,2}	CO ₂ free sites ^{1,2}	SO ₂ capacity (CO free sites)	SO ₂ capacity (CO ₂ free sites)
IBC-102, HNO ₃	---	5.12	1.4	0	0	---	---
IBC-102, HNO ₃ , 525°C	0.142	1.84	6.7	1.37	2.59	1.04	0.55
IBC-102, HNO ₃ , 725°C	0.376	0.50	12.8	3.35	2.94	1.12	1.28
IBC-102, HNO ₃ , 925°C	0.448	0.16	---	3.90	3.01	1.15	1.49
Calgon F400, HNO ₃	---	4.91	1.4	0	0	---	---
Calgon F400, HNO ₃ , 200°C	0.072	4.47	0.8	0.86	0.34	0.84	2.12
Calgon F400, HNO ₃ , 525°C	0.183	1.75	7.6	1.28	2.52	1.43	0.73
Calgon F400, HNO ₃ , 725°C	0.244	1.06	5.5	2.26	2.56	1.08	0.95
Calgon F400, HNO ₃ , 925°C	0.334	0.53	5.4	3.28	2.75	1.02	1.22

¹ moles/kg char.

² calculated assuming that 1 chemisorbed O₂ evolved as 2 CO during TPD is equivalent to 2 CO free sites, and 1 chemisorbed O₂ evolved as 1 CO₂ is equivalent to 1 CO₂ free site.

³ not determined.

⁴ CO₂ concentration below detectable limits.

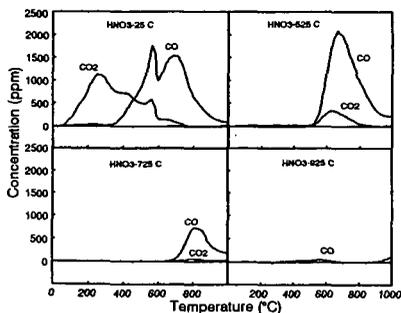


Figure 1. TPD profiles of nitric acid/thermally desorbed IBC-102 chars.

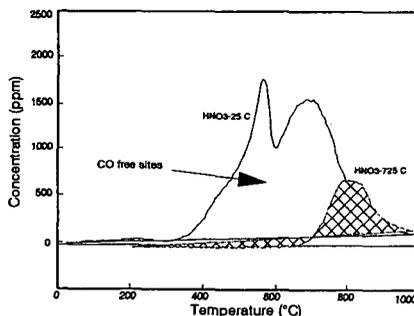


Figure 2. Subtraction of CO evolution profiles to determine CO free sites.

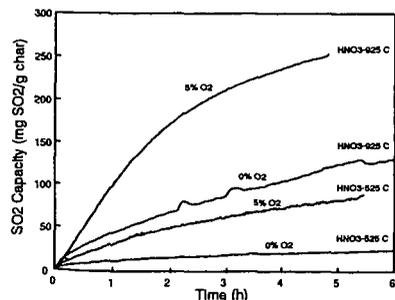


Figure 3. Effect of oxygen on SO₂ adsorption.

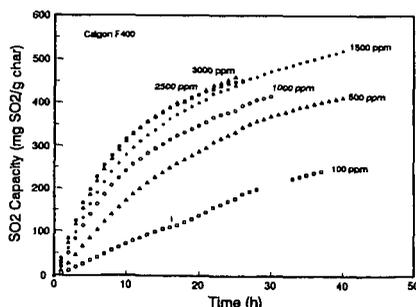


Figure 4. Effect of SO₂ concentration.