

NEW INSIGHTS ON THE MECHANISM OF SO₂ REMOVAL BY CARBON

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INTRODUCTION

In the presence of O₂ and H₂O, SO₂ is adsorbed on carbon at temperatures up to 200°C and converted to H₂SO₄ [1]. From a review of the literature, it is unclear whether the physical (surface area) [2,3] or chemical (oxygen content) properties [4,5] of a carbon determine its SO₂ capacity. It has been observed that SO₂ adsorption is directly related to the number of strongly basic functional groups on the carbon surface [4,5], although more recently it has been suggested that the presence of carbon surface oxides inhibits catalytic activity for adsorption of SO₂ and its conversion to H₂SO₄ [6,7]. Nevertheless, it appears that the nature and number of active sites is critical in determining SO₂ adsorption behavior of carbons [1,8], but to the best of our knowledge, no one has related SO₂ adsorption behavior directly to this fundamental property of carbon.

The initial objective of this study [9] was to determine whether Illinois coal is a suitable feedstock for production of activated char that could be used as a catalyst for removal of SO₂ from flue gas. A novel char preparation method was developed to produce activated char with SO₂ capacities greater than that of a commercial activated carbon [10-12]. A recent goal of the study has been to develop an experimental technique that could be used to explain or predict the SO₂ adsorption behavior of carbon. In this paper, initial findings are presented that use such a technique to measure active sites, and provide new insight into the mechanism of SO₂ removal by carbon.

EXPERIMENTAL

Chars were prepared from a 48x100 mesh Illinois No. 2, hvC bituminous coal, sample IBC-102 of the Illinois Basin Coal Sample Program [13]. The coal was physically cleaned prior to char production to reduce mineral matter content from 5.5 to 3.5%. The clean coal was pyrolyzed in N₂ at 900°C for 0.5 h in a 5-cm ID batch fluidized-bed reactor (FBR). Steam activation of the 900°C char was performed in a 2.5-cm ID FBR at 860°C in 50% H₂O/50% N₂ for 0.75 h to achieve 30% carbon conversion. The steam activated char and a commercial activated carbon, Calgon F400, were oxidized in a 45% nitric acid (HNO₃) solution at 80°C for 2.5 h. The H₂O activated/HNO₃ treated char and Calgon F400/HNO₃ treated samples are designated as Samples A1 and B1 in Table 1. To produce thermally desorbed chars, A1 and B1 were heated in N₂ to 525, 725, or 925°C and held for 1 h to remove carbon-oxygen (C-O) complexes formed by the HNO₃ treatment.

The kinetics of SO₂ adsorption was determined using a Cahn TG-131 thermogravimetric analyzer. A simulated flue gas containing 2500 ppmv SO₂, 5% O₂, 7% H₂O, balance N₂ at 120°C was used. Temperature programmed desorption (TPD) experiments were carried out in a flow-thru, 2.5-cm ID stainless steel fixed-bed reactor. A char sample (0.5 g) was heated in flowing N₂ (0.5 L/min) at 5°C/min to 1000°C and held for 1 h. Rosemount Model 880 CO and CO₂ non-dispersive infrared analyzers were used to monitor the concentrations of CO and CO₂ in the effluent gas.

RESULTS AND DISCUSSION

The authors [10] previously showed that, for chars prepared from IBC-102 coal under a wide range of conditions, there was no correlation between SO₂ adsorption capacity and N₂ BET surface area. In an effort to relate SO₂ adsorption behavior to other properties of the char, the nature and extent of oxygen functional groups on the char surface were studied by TPD. TPD profiles for sample A1 are shown in Figure 1. The CO and CO₂ evolution profiles of sample A1 show

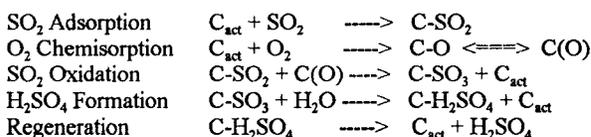
only slight overlap. Conceivably, to enhance SO₂ adsorption, this sample could be heated (in inert atmosphere) to a certain temperature, e.g., 525°C, to remove only the CO₂-forming functional groups and retain the CO-forming ones. The C-O groups that form CO upon thermal desorption are known to impart surface basicity, while C-O groups that form CO₂ are acidic by nature [14]. A carbon with a basic surface would be expected to adsorb more SO₂ [4].

Figure 1 also shows the TPD profiles of sample A1 thermally desorbed at 525, 725 and 925°C (Samples A2, A3 and A4). The corresponding kinetics of SO₂ adsorption curves are presented in Figure 2. The amount of SO₂ adsorbed increases with increasing thermal desorption treatment. Note that the char with the smallest amount of C-O complex (A4) adsorbed the largest amount of SO₂. This suggests that sites that form a stable C-O complex during char preparation are made available by the thermal desorption treatment, and that adsorption of SO₂ may preferentially occur at these free adsorption sites. Kisamori *et al.* [6,7] showed that heat treatment of activated carbon fibers to 800°C increased both the SO₂ oxidation rate and overall SO₂ capacity. They postulated that additional active sites were introduced on the carbon surface by thermal decomposition of C-O functional groups into CO and CO₂.

In our study, an effort was made to titrate those active sites responsible for SO₂ adsorption by integrating the TPD profiles presented in Figure 1. Figure 3 shows how the number of CO derived free sites for sample A3 can be estimated by subtracting the amount of CO evolved during TPD of sample A3 from the total amount of CO evolved during TPD of the original HNO₃ treated char, sample A1. The concentration of CO derived free sites is depicted by the shaded area in Figure 3. The same procedure can be used to determine the number of both CO and CO₂ free sites for each of the thermally desorbed samples listed in Table 1. A linear relationship (correlation coefficient of > 0.99) exists between the SO₂ adsorption capacity and total number of free sites as determined by TPD. It is interesting to note that there is nearly a one-to-one ratio between the CO free sites and SO₂ capacity (Table 1). Similar results are obtained for sample B1 (Table 1). To the best of our knowledge, this approach has never been used to explain quantitatively SO₂ removal by carbon.

Apparently, for these chars, formation of stable C-O complex during char preparation prevents adsorption of SO₂ onto otherwise active adsorption sites. Increasing the desorption temperature from 200 to 925°C removes an increasing amount of these stable C-O complexes, which creates nascent sites or "free sites" that are highly reactive towards SO₂ adsorption. In addition, removal of C-O complexes from pore entrances may allow more access of SO₂, O₂ and H₂O to the inner pore volume resulting in an increased SO₂ adsorption capacity. Note that, for the most part, higher desorption temperatures increase not only the total amount of SO₂ adsorbed, but also the initial rate of SO₂ adsorption (Figure 2). This could be due to a higher concentration of active sites believed to be responsible for controlling the initial rate of SO₂ adsorption in this regime [1].

The following mechanism for SO₂ removal by carbon is proposed to explain these results [11].



Adsorption of SO₂ and O₂ on carbon active sites (C_{act}) occur in parallel. The oxygen atom may form a reactive C(O) intermediate and/or stable C-O complex. Stable C-O complex formation is predominantly an inhibiting process (stable C-O complex deactivates the carbon catalyst); however, the mechanism implies that it can also be an intermediate step in SO₂ adsorption and conversion to H₂SO₄. The stable (unreactive) C-O complex, depending on its energy state and neighboring functional groups, can be transformed into a reactive C(O) intermediate (or fleeting complex). Catalytic oxidation of SO₂ to SO₃ involves reaction of SO₂ with this fleeting C(O) complex. Hartman and Coughlin [15] found the catalytic oxidation of SO₂ to SO₃ by carbon to be the rate determining step in the conversion of SO₂ to H₂SO₄. If the rate determining step is, indeed, catalytic oxidation of SO₂ to SO₃, the rate of SO₂ adsorption could be expressed as

$$d[\text{SO}_2]/dt = k [\text{C}(\text{O})] [\text{SO}_2]^n$$

where k is a rate constant (turnover frequency of the carbon catalyst) and n is the order of the reaction [11]. For concentrations of SO₂ less than 1500 ppmv, the reaction order was found to be between 0.5 and 1, and for concentrations of SO₂ greater than 1500 ppmv, the reaction order approached zero [11,12].

In the presence of water, SO₃ is converted to H₂SO₄. Water adsorbed in the pores may act to regenerate the carbon surface. When sulfuric acid adsorbed on the carbon surface readily goes into solution, the carbon active site can undergo numerous cycles of adsorption/desorption without external means of regeneration. The production of H₂SO₄ proceeds indefinitely until water adsorbed in the pores becomes saturated with H₂SO₄. At equilibrium (which may require more than 60 h to achieve [11,12]) the pore volume of the carbon defines its SO₂ adsorption capacity. An increase in the amount of SO₂ adsorbed with increasing thermal desorption temperature is due both to an increase in the concentration of the active sites and an increase in the available 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

Chars were prepared from Illinois coal by a novel nitric acid/thermal desorption treatment. An attempt was made to relate TPD data to observed SO₂ adsorption behavior. The formation of stable C-O complex during char preparation may have served only to occupy carbon sites that were otherwise reactive towards SO₂ adsorption. A fleeting C(O) complex was postulated to be the reaction intermediate necessary for conversion of SO₂ to H₂SO₄. SO₂ adsorption was directly proportional to the number of free adsorption sites on the carbon surface. The SO₂ capacity of a series of chars normalized with respect to the number of free sites varied by less than a factor of two, which indicated an excellent correlation. Based on these results, a new mechanism for SO₂ adsorption on carbon active sites and conversion to H₂SO₄ was proposed.

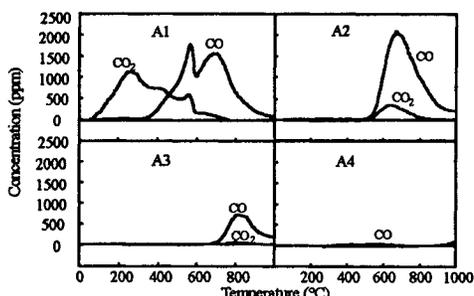


Figure 1. TPD profiles of HNO₃-treated IBC-102 chars desorbed at different temperatures.

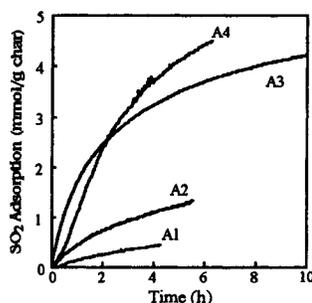


Figure 2. SO₂ adsorption on HNO₃-treated IBC-102 chars desorbed at different temperatures.

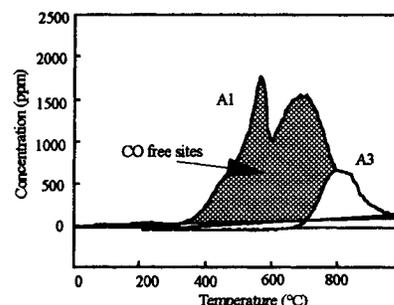


Figure 3. Depiction of number of free sites for sample A3, equal to the difference in number of initial CO-forming sites (Sample A1) and CO-forming sites for sample A3.

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Table 1. Variation of SO₂ adsorption with the concentration of free sites.

ID	Sample	SO ₂ adsorbed ¹	CO free sites ^{1,2}	CO ₂ free sites ^{1,2}	Total free sites	SO ₂ total free sites
A1	IBC-102, 900°C; H ₂ O, 860°C; HNO ₃	---	0	0	0	---
A2	A1 desorbed @ 525°C	1.42	1.37	2.59	3.96	0.36
A3	A1 desorbed @ 725°C	3.76	3.35	2.94	6.29	0.60
A4	A1 desorbed @ 925°C	4.48	3.90	3.01	6.91	0.64
B1	Calgon F400, HNO ₃	---	0	0	0	---
B2	B1 desorbed @ 200°C	0.72	0.86	0.34	1.2	0.60
B3	B1 desorbed @ 525°C	1.83	1.28	2.52	3.8	0.48
B4	B1 desorbed @ 725°C	2.44	2.26	2.56	4.82	0.51
B5	B1 desorbed @ 925°C	3.34	3.28	2.75	6.03	0.55

¹mmole/g char; ²calculated assuming that 1 mole O₂ evolved as 2 CO during TPD is equivalent to 2 CO-forming sites, and 1 mole CO₂ evolved as 1 CO₂ is equivalent to 1 CO₂-forming site; ³ not determined.