

ADSORBED MOLECULAR OXYGEN AND THE SURFACE BEHAVIOR OF SOOT

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INTRODUCTION

A role of adsorbed molecular oxygen in surface reactions of black carbon (in the form of n-hexane soot) has been observed. Countless articles on the surface structure and reactivity of solid carbon, including several from this group (1-5), have identified carbon-oxygen surface functionalities as underlying adsorption or reactivity characteristics of specific materials. This paper describes, rather, several cases in which reversibly adsorbed molecular oxygen directly participates in phenomena occurring at the carbon surface.

RESULTS AND DISCUSSION

Hydration

A dependence of the extent of its surface hydration on soot aging was first observed in microgravimetric studies of water adsorption as a function of relative vapor pressure (6). Separate experiments in which freshly-prepared soot samples were exposed to pure O₂ prior to hydration with others evacuated prior to hydration, revealed significantly more and less water adsorption, respectively, compared with the fresh soot itself. Application of a modified Dubinin-Radushkevich (DR) equation (7) to the data enabled the determination of surface coverage and mass adsorbed per gram at limiting adsorption, and also at the point at which activated adsorption is essentially complete (the chemisorption limit).

The adsorption data (mass increase and the relative water pressure, P/P₀) from these measurements were treated with the DR equation to yield the results summarized in Table I.

Table I. Effect of Oxygen Adsorption on Soot Hydration

| Soot | Limiting Adsorption gx10 ² /gs | θ _l * | Limiting Chemi- sorption gx10 ² /gs | θ _c * |
|-------------------------------|---|------------------|---|------------------|
| 24-hours | 1.76 | 0.80 | 0.507 | 0.223 |
| O ₂ - contacted | ± 0.01 | ± 0.02 | ± 0.004 | ± 0.004 |
| Fresh | 1.26 | 0.58 | 0.473 | 0.217 |
| | ± 0.01 | ± 0.01 | ± 0.005 | ± 0.005 |
| Evacuated | 0.966 | 0.44 | 0.440 | 0.202 |
| | ± 0.006 | ± 0.01 | ± 0.003 | ± 0.005 |

* Surface coverage using H₂O molecular area as 12.2Å² (8), where θ_l is at limiting adsorption and θ_c at the chemisorption limit.

As is evident from these data, adsorption of water by the soot increases with O₂ coverage of the soot surface. For example, the limiting surface coverage (θ_l) increases from 44% for evacuated fresh soot to 80% for the same material whose surface is saturated with O₂ at ambient temperature. Similarly, by comparing the adsorption of water at the chemisorption limit and at limiting adsorption, it is seen that the fraction of adsorbed water involving chemisorption decreases from about 46% to 29% as the surface O₂ increases. Since a smaller fraction of the (greater) adsorbate is involved in chemisorption on an O₂-saturated surface, a process involving the hydrolysis of

carboxylic functionalities, the adsorbed oxygen appears to be providing adsorption sites for water. A regular decrease in adsorbate affinity coefficient for water (6) with increased O_2 coverage, determined from the DR equation plot, further supports relatively more (weaker) H_2O-O_2 surface interactions.

Although the mechanism by which surface O_2 facilitates increased water adsorption is not yet clear, earlier experiments showed that it is properly described as physisorption (as opposed to activated adsorption). Figure 1 illustrates the effect of the sequential treatment of soot with flowing dry nitrogen, water

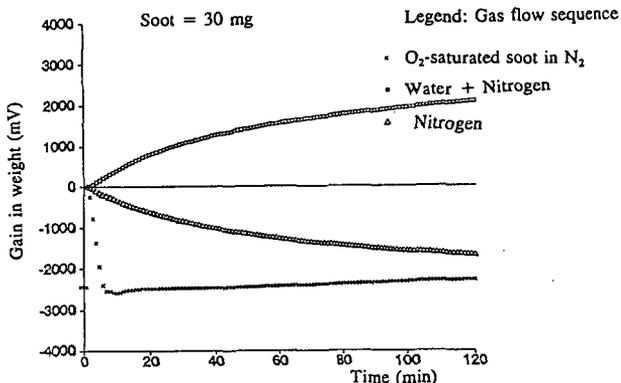


Figure 1. Study of desorption and adsorption of O_2 and H_2O on soot (6).

vapor plus nitrogen and then nitrogen again. Microgravimetric measurement of mass change reveals a rapid substantial loss when an O_2 -saturated sample is subjected to flowing nitrogen, apparently most of it the loss of physisorbed O_2 . Subsequent to resetting the microbalance, treatment with water vapor plus nitrogen, and then flowing nitrogen again shows the usual hydration pattern and removal of water adsorbate, respectively. Considerable quantities of molecular oxygen may be adsorbed on freshly-prepared n-hexane soot and are involved in the water adsorption by, and hydration of, the soot surface.

EPR Studies

The observation by EPR of significant concentrations of unpaired electrons in n-hexane soot(1), consistent with their existence in coals and other graphitic carbonaceous materials, suggested the use of spin density as a probe of the behavior of adsorbed molecular oxygen which is paramagnetic. The effect of adsorbed O_2 is to increase the width and to decrease the intensity of the EPR spectrum of soot, changes reflected in an increased peak-to-peak line width, decreased peak height, and decreased normalized integral of the single absorption having a g value of 2.0046. Accordingly, series of replicate measurements using X-band CW EPR on freshly prepared soot samples were carried out. These samples, attached to the vacuum line through a special manifold within a heating mantle, were evacuated at $100^\circ C$ in the 10^{-4} torr range overnight before exposure to accurately measured pressures of pure O_2 . Figure 2A is a plot of the corrected normalized integral (CNI) versus P_{O_2} , where the error bars represent the standard deviation of individual measurements. The CNI for soot evacuated in this manner, before addition of O_2 , is $(1.62 \pm 0.07) \times 10^7$. The linear relationship between spin density and physisorbed O_2 (assumed proportional to gas phase pressure) over the pressure range from 0 to 35 torr demonstrates not only the interaction between the unpaired electron spins of molecular

oxygen and soot, but also provides a means of monitoring the surface behavior of O_2 during adsorption or reaction.

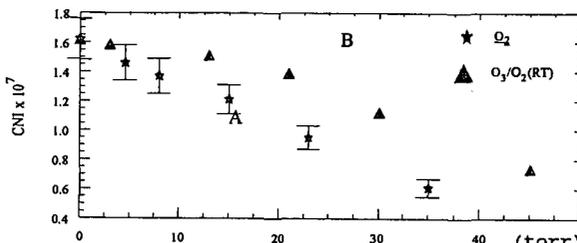


Figure 2. Effect of O_2 on the EPR signal of soot.

The Ozone-Soot Reaction

A detailed study (9) of the reaction between n-hexane soot and ozone at low concentrations has revealed a role of adsorbed molecular oxygen. This complex reaction involves essentially three stages. Following a fast initial catalytic decomposition of O_3 , a rapid soot mass increase accompanied by CO_2 and H_2O formation is itself followed by a long period of soot oxidation in which the rate of O_3 loss is second order in O_3 (9). It is during the second stage of this reaction that material balance calculations, based upon careful analysis of products and reactants, reveal an involvement of O_2 in that stage. Expressing the oxygen atom content of reactants and products in micromoles, the overall reaction results in a net loss of O_3 oxygen (as O_2 from catalytic decomposition) in the amount of about 20% which does not yield measurable O-containing product. During this second stage of the reaction, from 2.5 to 30% of reaction, however, the O atom gain in products averages 70%, a gain which is not from O_3 oxygen.

A plot of CNI of the soot EPR spectrum versus gas pressure (1.5% O_3 in O_2) is Figure 2B, to be compared with the same plot for O_2 alone (Figure 2A). At lower pressures, the rate of spin density decrease with increased O_3/O_2 is much less than with O_2 alone, while beyond 20 torr the slopes of the two plots are essentially the same. These data appear to confirm the consumption of a fraction of the O_2 in a reaction which does not leave it for physisorption. A plausible interpretation is that the rapid reaction with O_3 , actually probably O atom from its dissociation, yields fragments on the carbon surface which are reactive with O_2 . The soot is not similarly reactive with O_2 alone under ambient conditions. We are not aware of other such examples of physisorbed O_2 involvement in surface reactions of black carbon. To the extent that soot "aging" is an annealing of the surface by physisorbed O_2 , this effect also must underlie the difference in rate laws for the O_3 -soot reaction (9) between freshly prepared and aged soot; for example,

$$\begin{aligned} \text{Initial rate} &= k[O_3](\text{soot})^{1/2} & (1) \\ \text{versus} & & \\ \text{Initial rate} &= k'[O_2] + k''(\text{soot}) & (2) \end{aligned}$$

respectively.

Other Adsorptions

SO_2

Because of the likelihood that adsorbed molecular O_2 plays a role in other soot surface reactions, in the manner discovered for the O_3 reaction, our studies of adsorption on soot also have included O_2 as adsorbate. The rapid oxidation of SO_2 at the soot surface which requires the presence of O_2 and H_2O , for example,

is one important case. The coadsorption of O₂ and SO₂ on n-hexane soot has been examined in detail.

Figure 3 shows the gain in mass of 10 mg soot as a function of

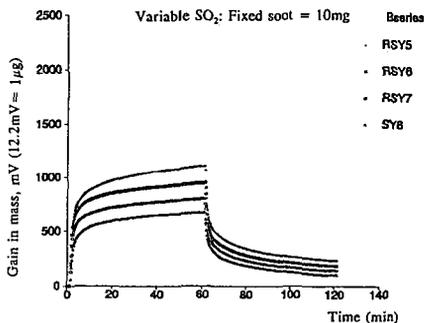
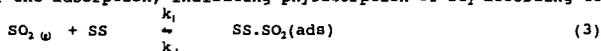


Figure 3. Adsorption of SO₂ on soot.

time in the presence of 606, 1010, 1515, and 2020 ppm SO₂. These were flow experiments in which the medium was zero air. At 60 minutes, the SO₂ flow was stopped and the microgravimetric cell (6) continued to purge with the zero air alone. The rapid loss of SO₂ from the surface follows a pattern which is the inverse of the adsorption, indicating physisorption of SO₂, according to



$$K = k_1/k_{-1} = [\text{SS} \cdot \text{SO}_2(\text{ads})] / [\text{SO}_2(\text{g})][\text{SS}] \quad (4)$$

where SS = surface site for SO₂.

From 85 to 79 percent of the SO₂ behaves in this manner, respectively, as indicated by the asymptotic approach of the microgravimetric curve to a limiting mass value greater than the initial. Another pathway, probably surface hydration and possibly oxidation, apparently exists for SO₂ as well; water molecules cannot be rigorously excluded from the surface under these conditions.

The coadsorption of SO₂ and O₂ were studied by EPR, and the results are summarized in Figure 4. No effect of SO₂ on the

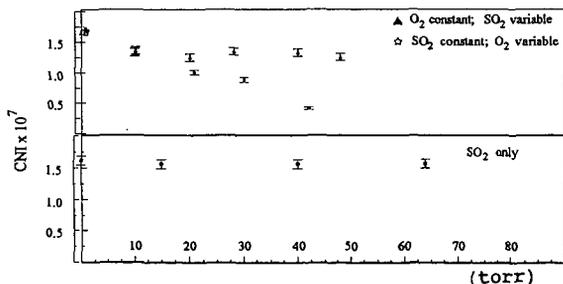


Figure 4. Effect of SO₂ on soot.

normalized integral of soot's EPR signal is observed, this lack of effect extending to 10⁷ ppm. (The small decline from the 1.62

is due to a trace of O_2 in the SO_2 sample). The significance of this study is to be found in the fact that 1) O_2 has the same effect on the spin density of soot on which SO_2 is physisorbed as it does on pure soot, and 2) at a constant O_2 coverage, SO_2 has no effect; no O_2 is displaced by SO_2 . This suggests that surface oxidation of SO_2 by O_2 does not occur measurably at these surface coverages. Either O_2 and SO_2 do not compete for the same sites or the soot surface- O_2 interaction is stronger than that between soot and SO_2 . Calculations based on the specific surface of n-hexane soot ($89m^2/g$), masses of O_2 and SO_2 adsorbed per gram of soot under the experimental conditions, and established surface areas for the adsorbed molecules (19.2 \AA^2 for SO_2 (10), 14.1 \AA^2 for O_2 (11)), indicate that SO_2 occupies nearly the same fraction of the surface (~18%) that O_2 (~20%) does, which means that about 1/3 less SO_2 molecules than O_2 are adsorbed per unit mass of soot under the conditions of zero air (125 torr O_2) and 2000 ppm SO_2 . In the case of paramagnetic O_2 , the surface coverage is no doubt governed by the surface density of soot's unpaired electrons, where the SO_2 is not influenced by that factor.

NO and NH_3

Evidence of the effect of adsorbed molecular O_2 on the adsorption of both NH_3 and NO has been found as well. These molecules, unlike the reversibly adsorbed SO_2 species, compete with O_2 for surface sites. Microgravimetric studies of NH_3 adsorption at higher concentrations, carried out in a variety of gas phase environments, reveal this competition which probably has its origin in the hydrogen bonding capacity of NH_3 . EPR studies of the competition of NO and O_2 for unpaired electron sites on soot clearly show a surface interaction between NO and O_2 as well. Experiments on both of these systems continue.

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