

THE ROLE OF SUBSTITUTIONAL BORON IN CARBON OXIDATION: INHIBITOR AND CATALYST

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KEYWORDS: carbon oxidation, inhibition, catalysis, boron.

INTRODUCTION

Carbon oxidation has been very thoroughly investigated. It is a reasonably well understood heterogeneous gas/solid reaction [1-4]. Yet there are many practical and fundamental 'details' that need to be sorted out. There are also some very important fundamental issues that are not understood. Others may want to add (or subtract?) some issues, but here is our list of key outstanding questions in the C/O₂ reaction:

- (a) What is the exact nature of the relation between 'reactive' C(O) intermediates and 'stable' C-O complexes on the carbon surface?
- (b) What is the reason for the commonly observed "compensation effect" in both uncatalyzed and catalyzed carbon gasification?
- (c) Which structural features of the carbon surface govern the magnitude of the CO/CO₂ ratio in the products of oxidation and, in particular, how is CO₂ formed?
- (d) Is it possible that, when carbon is doped with boron, both a catalytic and an inhibiting effect can be observed?

A companion paper presented at this symposium [5] addresses issue (c). The present communication deals with issue (d). Reference 6 had roughly the same title as this paper, but it ended with a question mark. In the macroscopic world, in contrast to the quantum world [7], mutually exclusive phenomena are not commonly thought to coexist. So boron is considered to be either an inhibitor or a catalyst of carbon oxidation, but not both. Here we provide additional arguments for this remarkable influence of boron on the oxidation of a wide range of carbonaceous solids (and we thus replace the question mark with an exclamation point). Elsewhere [7] we address issues (a) and (b); in particular we argue that both the elusive concept of the compensation effect and the intriguing balance between reactive and stable carbon-oxygen surface complexes may have an analogous explanation to the one offered here for the role of boron in carbon oxidation.

Boron is considered to be one of the very few promising candidates for chemical protection of carbon/carbon composite materials against oxidation. Oxidation protection is of paramount importance for the use of these strategic materials in demanding (e.g., structural) aerospace applications. (Most ceramic coatings have a thermal expansion mismatch with carbon and thus develop cracks which lead to carbon exposure to high-temperature O₂.) The conventional wisdom is that boron inhibits carbon oxidation. Its inhibiting effect can be manifested in three different ways: (a) Substitutional boron enhances the graphitization of carbon [8-10]. (b) As the surface carbon atoms are consumed, substitutional boron forms an oxide surface film, which acts as an O₂ diffusion barrier and an active site blocker [9,11-14]. (c) Substitutional boron redistributes the π electrons in the basal plane (graphene layer), lowers the Fermi level of carbon, and hence presumably inhibits the desorption of CO and CO₂ [9,11,14]. This last mode of inhibition is of great fundamental interest; it had not been verified in the past. As a consequence of our recent results [6], and upon closer examination of some early studies, its closer scrutiny is warranted. We provide such a scrutiny in the present communication.

EXPERIMENTAL

Three widely differing carbon materials were used: a heat-treated ('graphitized') carbon black (Graphon, Cabot Corp.), Saran char (produced by pyrolysis of a PVC/PVDC copolymer manufactured by Dow Chemical Co.) and a glassy carbon (a phenolic-resin-derived material, Alfa-Aesar). Boron was introduced substitutionally into the quasi-graphitic lattice by heating these carbons, physically mixed with boron powder (99.999%, Alfa-Aesar) at different levels (1, 2 and 5 wt % B), to ~2450 °C in Ar [6,15]. Some loss of boron occurred during this treatment (see Results).

Isothermal carbon oxidation experiments (~10 mg samples; 1 atm; 21% dry O₂, 99.994%; 250 cc/min) were performed with these samples in a Mettler TGA. The reaction temperature was achieved after heating the sample in N₂ at 25 °C/min; negligible gasification occurred during this nonisothermal period [15]. In selected cases, the reactive surface area (RSA) [16] of the carbons was determined using a commercial transient kinetics apparatus (SSITKA 2000, Altamira Instruments). The

integrated area under the transient decay curves for CO and CO₂, after switching from O₂ to inert gas at different conversion levels, was used as a first approximation to true RSA values.

RESULTS

Figure 1 shows that boron acts as a catalyst of oxidation of glassy carbon. Figure 2 summarizes the kinetic data (at the same carbon conversion level) for the boron-doped polymer-derived carbons. In agreement with the behavior observed for boron-doped Graphon [6], boron is seen to act as a catalyst at low boron loadings and as an inhibitor at higher boron loadings. The global activation energy does not seem to depend in a consistent way on boron content. It is governed rather by the nature of the carbon: as almost invariably reported in the literature, it increases as the degree of crystalline perfection of the carbon increases (33±3 kcal/mol for undoped and boron-doped Saran char vs. 44±5 kcal/mol for undoped and boron-doped Graphon).

Figure 3 shows the x-ray diffraction profiles for undoped and boron-doped Saran chars. At the highest boron loadings, the signature of enhanced graphitization - splitting of the {10} turbostratic peak (at ~43 °2θ) into {100} and {101} graphitic peaks (at ~42 °2θ and ~44 °2θ) - is observed.

Figures 4 and 5 summarize the catalytic and/or inhibiting effects of boron in carbon oxidation as a function of the reaction temperature and the extent of reaction (percent carbon conversion). In agreement with the data shown in Figure 2 and in our earlier work [6], the net effect depends on the concentration of boron in the carbon. It is surprising that boron, present presumably as substituent atoms in the carbon lattice, acts as a catalyst at low loadings and as an inhibitor at higher loadings. This is in contrast to all other reports in the literature [11,12,14], where an inhibiting effect was found at all boron concentration levels when dry O₂ was used as the reactant. Interestingly, Thomas and Roscoe [17] observed a catalytic effect in moist oxygen. More recently, Rodriguez and Baker [18] confirmed the inhibiting effect of the boron oxide, but reported a catalytic effect of boron carbide.

In summary then, all our experimental results obtained to date show that boron inhibits carbon oxidation at high initial boron loadings, high temperatures and high carbon conversion levels. In contrast, boron catalyzes carbon oxidation at low initial loadings, low temperatures and low conversion levels. Additional results [15] suggest that boron is an inhibitor of oxidation at low O₂ partial pressures and a catalyst at higher pressures.

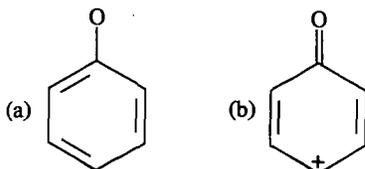
DISCUSSION

In light of the foregoing results, the premises on which some of the earlier work was based [9,11,14] need to be reexamined.

There is no doubt that boron catalyzes the graphitization of a wide range of carbons. (Figure 3 and our other results [15] confirm this well known effect.) This in turn leads in general to a decrease in carbon reactivity [19] and thus, effectively, to oxidation inhibition.

On the basis of results shown in Figures 4 and 5, there is no compelling reason to doubt either that B₂O₃ is formed upon oxidation of boron-doped carbons [17]. It is worth noting, however, the recent work by Cermignani et al. [20] in which X-ray photoelectron spectroscopy was used to identify the boron-containing species after heat treatment and oxidation of boron-doped CVD carbon films. After oxidation at 600 °C for 4 h, they saw no clear evidence that B₂O₃ was the predominant species formed; instead, they identified boron oxycarbides as the dominant surface species.

What needs reevaluation is the proposed [9] electronic effect of boron (mechanism (c) in the Introduction). Its origin lies in the electronic effect of a carbon gasification catalyst which, upon oxygen adsorption, induces type (b) distribution of the π electrons in the graphene layer [21]:



By accepting electrons from the graphene layer (e.g., into unfilled d bands of a transition metal), a catalyst is thought to facilitate both O₂ adsorption (by increasing the C-O bond strength) and product desorption (by weakening the adjoining C-C bonds, as illustrated above).

In contrast to the oxygen-transfer theory [22], the electron-transfer theory of catalysis [23] has not found much support in the carbon gasification literature and had not been confirmed experimentally. Nevertheless, a recent theoretical study of potassium-catalyzed graphite oxidation [24] does indicate that this electron-donating catalyst lowers the work function of graphite and thus enhances the dissociation probability of O₂ on the surface. This is opposite to the well known electronic effect of substitutional boron, which does not contribute electrons to the delocalized π system of the graphene layer and lowers the Fermi level of graphite [12]. Boron would thus be expected to decrease, to some extent at least, the dissociation (chemisorption) probability of O₂. Indeed, Allardice and Walker [12b] concluded that boron inhibits the chemisorption of CO₂ in the C/CO₂ reaction.

This redistribution of π electrons in the presence of substitutional boron results not in the weakening of C-O bonds and strengthening of C-C bonds [9], but in exactly the opposite effect (see figure above): being essentially an electron 'acceptor', as discussed above, boron is predicted to induce type (b) distribution of π electrons and thus weaken C-C bonds and strengthen C-O bonds. This trend was confirmed by a straightforward application of Hückel molecular orbital theory [15]. In fact, Allardice and Walker [12a] used this argument, together with the observed decrease in the activation energy for oxidation of graphite, to anticipate the *catalytic* effect of substitutional boron (even though in their study this effect was masked and overwhelmed by the inhibiting effect of B₂O₃).

Substitutional boron thus emerges as *both* a catalyst and an inhibitor of carbon oxidation. The catalytic effect is clearly observed for the first time; this is attributed to the fact that samples possessing relatively high surface areas were used, and the catalytic effect was not masked by the ubiquitous inhibiting effect of B₂O₃. The fact that boron is a catalyst under conditions favoring desorption control (low temperature and high oxygen partial pressure) and inhibitor under conditions favoring adsorption control (high temperature and low oxygen partial pressure) is quite intriguing. It suggests that this phenomenon is yet another example of the well known 'compensation effect', which we tentatively interpreted [7] as a 'macroscopic complementarity principle': in the presence of substitutional boron the turnover frequency for carbon atom removal increases (due to the catalytic effect of C-C bond weakening), but the number of reactive sites decreases (due to the inhibiting effect on O₂ adsorption). The latter point is illustrated in Figure 6.

ACKNOWLEDGMENTS

This study was made possible by financial support from the U.S. Air Force Office of Scientific Research (AFOSR URI F49620-93-1-0311, Major T. Erstfeld, Project Manager). Fruitful collaboration with G. S. Rellick (The Aerospace Corporation, El Segundo, CA) is also acknowledged. A partial SSITKA equipment grant was received from Altamira Instruments.

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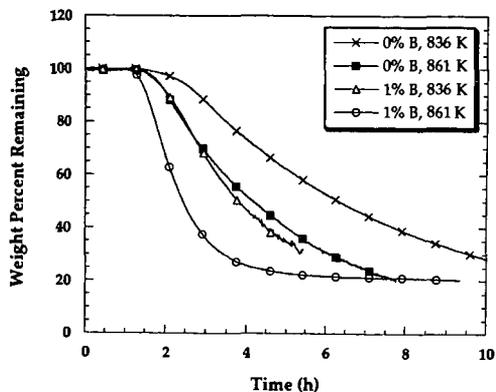


Figure 1. Typical TGA plots for boron-free and boron-doped glassy carbon.

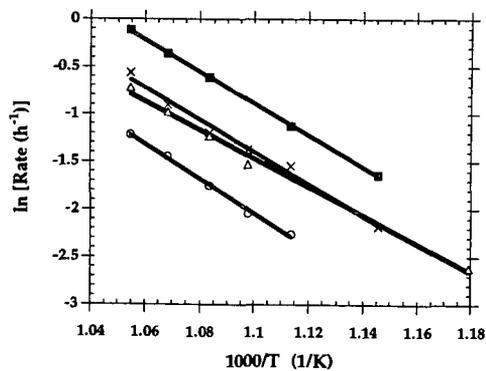


Figure 2. Arrhenius plots for Saran char doped with different amounts of boron and gasified at 1 atm (21% O₂): x, 0% B, 33 kcal/mol; ■, 1.1% B, 33 kcal/mol; △, 1.9% B, 30 kcal/mol; ○, 3.8% B, 36 kcal/mol.

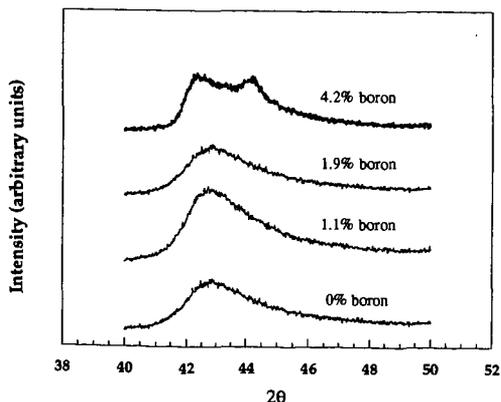


Figure 3. X-ray diffraction patterns for Saran char doped with different concentrations of boron.

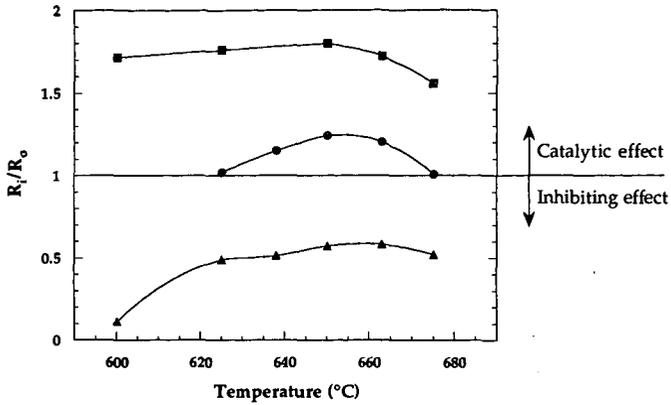


Figure 4. Effect of reaction temperature on the inhibition effect of boron-doped Saran char for various levels of initial boron concentration: ■, 1.1% B; ●, 1.9% B; ▲, 3.8% B. (R_i and R_0 are the reaction rates for doped and undoped samples.)

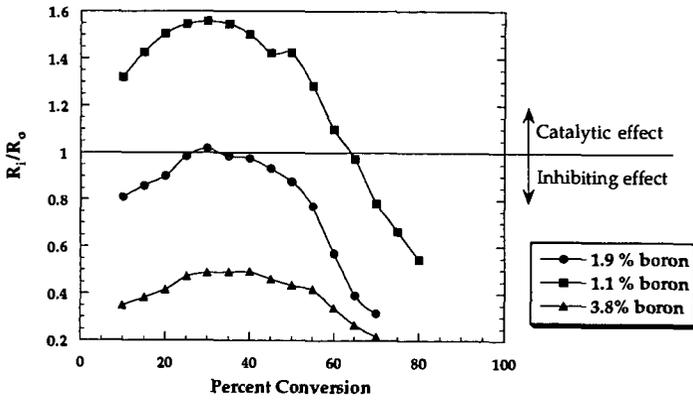


Figure 5. Effect of conversion level on the inhibition effect of boron-doped Saran char for various levels of initial boron concentration. (R_i and R_0 are the reaction rates for doped and undoped samples.)

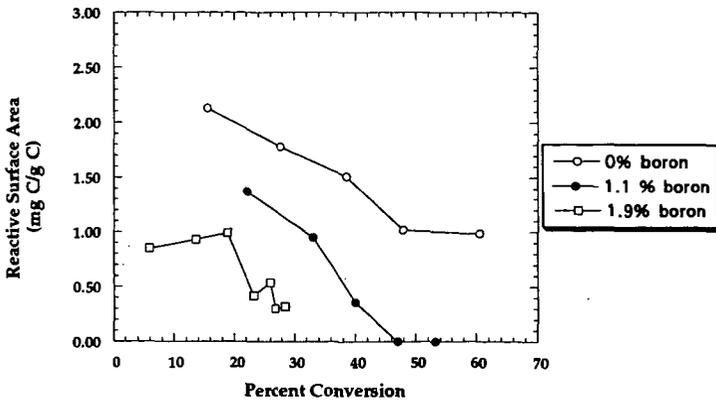


Figure 6. Reactive surface area vs. conversion for Saran char doped with boron: ○, 0% boron; ●, 1.1% B; □, 1.9% B. (RSA estimated at 700 °C and 1 atm, 5% O_2 .)