ROLE OF SUBSTITUTIONAL BORON IN CARBON OXIDATION

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Introduction

It has been shown in numerous investigations that boron additives are effective inhibitors of carbon oxidation [1-5]. However, both catalytic and inhibiting effects of boron on carbon oxidation have also been reported [4,5]. The inhibiting effect is most often attributed to the formation of protective B_2O_3 coating upon carbon oxidation, and not to an intrinsic inhibition by surface B atoms in the lattice. Catalysis of carbon graphitization and electron-transfer effects have also been invoked [3]. While the evidence for the former is readily available, the electron transfer mechanism has not been clear [5]: substitutional boron is assumed to be an electron acceptor, it presumably reduces the electron density at the carbon crystallite edges and thus decreases the probability of dissociative oxygen chemisorption [3]. However, this electron 'acceptor' character of boron has been interpreted also as weakening C-C bonds and strengthening C-O bonds and thus being responsible for a catalytic effect on carbon oxidation [4,5].

The objective of this paper is to attempt to resolve this contradiction by directly determining the changes in electron density of carbon atoms due to the presence of substitutional boron. The effects on the activation energy of carbon-carbon bond cleavage were also studied.

Method

A seven-ring carbon structure was chosen as a model of the carbon crystallite surface (Figure 1). A boron atom was placed substitutionally in positions #16, #20 and #23. Calculations of free valence (FV) were performed by two different methods: (a) simple Hückel molecular orbital (HMO) method using the HMO-plus 1.5.1 program [6]; (b) semiempirical AM1 method using the MOPAC 5 program [7]. The activation energy for C–C bond cleavage was estimated with the aid of the AM1 method according to the procedure described in detail elsewhere [8].

Results and Discussion

Some of the key results of the calculations are summarized in Table 1. Interestingly, the FV on the carbon atoms is predicted to increase or decrease in the presence of boron, depending on their exact position with respect to the boron atom. Both methods show an increase in the total FV on the edge atoms (with the exception of boron at position #20, for which the AM1 method predicts a decrease). This result does not agree with the electron acceptor argument [3] which is often echoed in the literature. Rather, in agreement with straightforward electronegativity arguments, it suggests that trivalent boron induces a redistribution of the π electrons in such a way that, although the FV may decrease on some carbon atoms, the total FV on carbon edge sites increases.

Substitutional boron atoms do not contribute electrons to the π system of the graphene layers; they forms only three single σ-bonds with surrounding carbon atoms. Indeed, the calculations confirmed that (with an accuracy of ± 0.03) the order of the C–B bond is unity. As a result, π electron density increases on the carbon atoms that are adjacent to the boron atom. In other words, boron induces a redistribution of π electrons which leads to increasing electron density on carbon atoms at crystallite edges.

Because oxygen chemisorption can be thought of (at least to a first approximation) as an electrophilic addition process, active carbon sites with higher FV will preferentially chemisorb O_2. Therefore, a higher concentration of C(O) complexes is expected to exist on the surface containing sites with higher FV. Since the rate of carbon gasification is proportional to the concentration of C(O) complexes, the surface sites with higher FV will be gasified faster. Therefore, boron may indeed behave as a catalyst of carbon oxidation. The experimentally observed inhibition of oxidation in boron-doped carbons cannot be attributed to electron transfer effects; it appears to be primarily due to the formation of a B_2O_3 film which acts as an effective oxygen diffusion barrier. This is supported by the experimental fact that the inhibiting effect has been observed at high boron loadings (when complete surface coverage with such a coating is more likely), while at low loadings a catalytic effect is sometimes observed [4,5].

Another important practical conclusion can be drawn from these results: the presence of additional FV at the edges of carbon crystallites in the presence of substitutional boron increases reactivity on the edges and promotes the probability of crystallite growth in the horizontal (ab) direction. This argument is consistent with the experimentally observed fact that the catalytic effect of boron in carbon graphitization is often such that L_a increases very significantly, and often preferentially with respect to L_c [9].

These results can also explain the CO/CO_2 ratio behavior during the oxidation of boron-doped carbons. In particular, they can explain the literature reports that the relative amount of CO, with respect to CO_2, decreases for boron-containing carbons [2,10]. The CO/CO_2 ratio is known to be inversely proportional to the surface

concentration of C(O) complexes [8]. Since it was shown by calculations that boron catalyzes O_2 chemisorption, the boron-doped carbon is expected to have a higher oxygen concentration on the surface and, consequently, a lower CO/CO_2 ratio in the products of its oxidation.

The activation energy of the C_{19}-C_{20} bond cleavage with oxygen atom attached to the carbon atom #19 was estimated. It was 66 kcal/mol for the boron-free structure, and 60 and 69 kcal/mol when boron was placed in positions #20 and #16, respectively. Taking into account that the average accuracy of MOPAC calculations is ~5 kcal/mol, we conclude that the activation energy is not affected by boron. Therefore, the redistribution of electronic charge does not seem to affect the stability of the C–C bond, and it may not have a pronounced effect on the desorption step of carbon oxidation.

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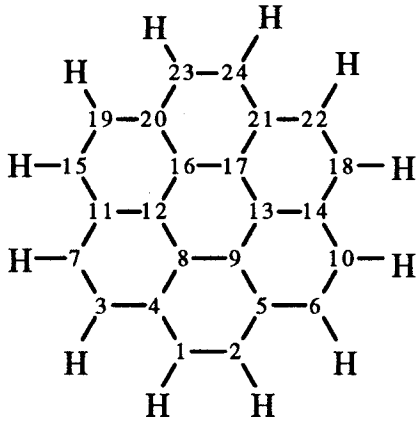

Figure 1. Model carbon structure.

Table 1. Free valence data for different model structures (see Figure 1).

Atom number	HMO				AM1			
	No B	B at #20	B at #16	B at #23	No B	B at #20	B at #16	B at #23
1*	0.449	0.478	0.469	0.453	0.288	0.333	0.290	0.288
2*	0.449	0.449	0.450	0.472	0.288	0.292	0.297	0.290
3*	0.449	0.494	0.477	0.453	0.288	0.239	0.269	0.245
4	0.118	0.122	0.128	0.134	0.238	0.348	0.240	0.284
5	0.118	0.146	0.141	0.118	0.238	0.257	0.231	0.242
6*	0.449	0.449	0.450	0.484	0.288	0.292	0.298	0.302
7*	0.449	0.470	0.480	0.460	0.288	0.268	0.281	0.295
8	0.150	0.155	0.148	0.153	0.222	0.229	0.209	0.227
9	0.150	0.158	0.160	0.152	0.222	0.216	0.291	0.230
10*	0.449	0.478	0.469	0.453	0.288	0.333	0.291	0.292
11	0.118	0.147	0.119	0.126	0.238	0.342	0.231	0.225
12	0.150	0.147	0.158	0.156	0.222	0.222	0.324	0.221
13	0.150	0.155	0.148	0.153	0.222	0.229	0.209	0.230
14	0.118	0.122	0.128	0.146	0.238	0.348	0.240	0.265
15*	0.449	0.461	0.528	0.473	0.288	0.163	0.472	0.314
16	0.150	0.202	-	0.143	0.222	0.416	-	0.247
17	0.150	0.147	0.158	0.190	0.222	0.222	0.324	0.306
18*	0.449	0.494	0.477	0.451	0.288	0.239	0.269	0.296
19*	0.449	0.472	0.442	0.455	0.288	0.249	0.334	0.258
20	0.118	-	0.200	0.149	0.238	-	0.402	0.361
21	0.118	0.147	0.119	0.117	0.238	0.342	0.231	0.254
22*	0.449	0.470	0.480	0.473	0.288	0.268	0.281	0.316
23*	0.449	0.472	0.442	-	0.288	0.249	0.334	-
24*	0.449	0.461	0.528	0.563	0.288	0.163	0.472	0.572
Σedges	5.388 4.939[a]	5.648 5.176[a]	5.692 5.250[a]	5.190[a]	3.456 3.168[a]	3.088 2.839[a]	3.888 3.554[a]	3.468[a]

*edge atoms; [a]calculated without atom #23.