INHIBITION OF CATALYTIC CARBON OXIDATION BY BORON AND PHOSPHORUS

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Introduction

Potassium and calcium salts are well known catalysts for the reaction between carbon and O_2[1]. Current airport runway deicing agents typically use formulations containing alkali or alkaline-earth metals (see *C&E News*, 01/01/01, p. 30). Very effective oxidation protection of aircraft brakes is thus of great practical and fundamental interest. Phosphorus[2,3] and boron compounds[4,5] are known to inhibit uncatalyzed carbon oxidation, but the relative effectiveness of these inhibitors in the presence of catalysts has yet to be demonstrated. Recently, phosphorus has been shown to improve the resistance of C/C composites to catalytic oxidation[6,7]. In the present study, the effects of B and P on the oxidation of C/C composites catalyzed by K or Ca acetate are evaluated by temperature-programmed oxidation (TPO).

Experimental

Samples of a commercial C/C composite aircraft brake (C2110, courtesy of Dr. Terry Walker, AlliedSignal Corp.) were used. They were cut into $(6\pm1)\times(6\pm1)\times(2\pm1)$ mm^3 pieces with a diamond saw. Before impregnation with inhibitors or catalysts, the samples were washed with de-ionized water. A methanol solution of methyl-phosphonic acid (98% purity, Alfa) was used to load P; the samples were then dried overnight at 110 ^{o}C and heated in N_2 at 600 ^{o}C for 2 h. A high-temperature treatment (2500 ^{o}C, Ar atmosphere) of samples with boron carbide (Aldrich) was used to incorporate boron into the carbon lattice[5].

Carbon impregnation with the catalyst was effected by immersing the samples into a saturated aqueous solution of potassium acetate (KAC) or calcium acetate (CaAC). Samples were then dried in an oven at 110 ^{o}C overnight. Catalyst loading was controlled by varying the solution concentration and was determined by the weight difference before and after impregnation; it is reported as weight percent of KAC or CaAC. Sample designation is as follows: C2N represents the pristine sample, suffix C or K denotes use of CaAC or KAC, while suffix P or B denotes P- or B-doping. For example, C2NPC represents a P-doped C2N sample subsequently impregnated with Ca.

In the TPO experiments (1 ^{o}C/min, 300 cm^3/min extra dry oxygen at 1 atm), a fixed-bed reactor connected to non-dispersive IR analyzers (Beckman, Model 864) for continuous monitoring of CO and CO_2 was used. The reactivity of the samples was calculated from the release rates of these gaseous products.

Results and Discussion

The magnitude of the catalytic effect of K and Ca is illustrated in Figure 1. For the essentially non-porous composite materials, it is sensitive to metal loading; in some cases even inhibition (due to encapsulation) was observed. The greater effectiveness of K is due not only to its higher loading (as a consequence of greater retention by the carbon sample) but also to its more facile decomposition/reduction on the carbon surface (ca. 585 K, vs. ca. 650 K for CaAC).

A comparison of the reactivity of P- and B-doped samples with that of the pristine material is presented in Figure 2. The greater degree of inhibition in the presence of P may be due to a much higher P loading; the relative effects of substitutional and surface-bound boron are known to be a complex function of substrate nature, B loading and reaction conditions[8].
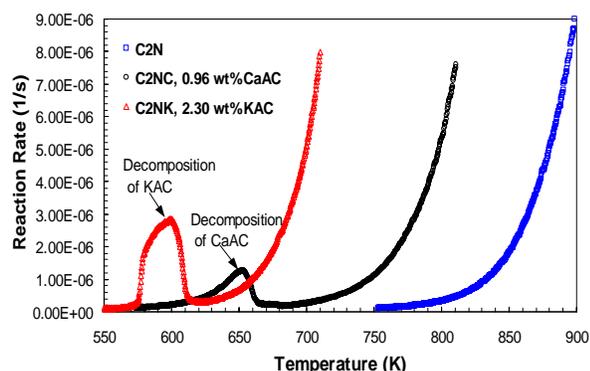
The TPO profiles of inhibitor-doped samples in the presence of catalysts are shown in Figures 3 and 4. The inhibiting effects are still seen in the presence of K or Ca, but they are significantly reduced, especially for the K-catalyzed reaction. Even more intriguing is the observation that, under the present conditions, B has a stronger inhibiting effect than P in Ca-catalyzed oxidation, whereas P is slightly more effective than B in K-catalyzed oxidation. Two potentially conflicting phenomena are thought to be responsible for these effects. On one hand, K is known to possess good wetting characteristics and mobility on the carbon surface, while Ca does not. On the other hand, the two inhibitors also interact differently with the carbon surface. At 600 ^{o}C, the phosphorus-containing inhibitor appears to be well dispersed and it would protect the carbon active sites more effectively. In contrast, use of B_4C to add substitutional B (with its very high melting point, 2350 ^{o}C) apparently results in the formation of a less evenly distributed protective layer after heat treatment at 2500 ^{o}C. The SEM observation of B-doped samples (Figure 5) suggests the presence of such a layer. Obviously, unless substitutional boron is very effective in suppressing O_2

chemisorption (which is not always the case[8]), the presence of a carbon-encapsulating protective layer is necessary for most effective oxidation inhibition. Such a layer serves not only as a diffusion barrier for O_2 access to the carbon active sites, but also interferes with the maintenance of good interfacial contact between the catalyst and the carbon substrate, which is essential for effective oxygen-transfer catalysis. This mode of inhibition is less effective in the case of K-catalyzed oxidation, because the potassium-containing active species can migrate into spaces between the B_4C layer and the carbon substrate and can thus maintain good interfacial contact. It will be interesting to evaluate the relative inhibiting effects of boron and phosphorus under conditions of equally favorable formation of a protective layer; in such a case the relative propensity for the formation of the (presumably inactive) phosphates and borates may dictate the degree of oxidation protection of aircraft brakes exposed to conventional deicing agents.

References

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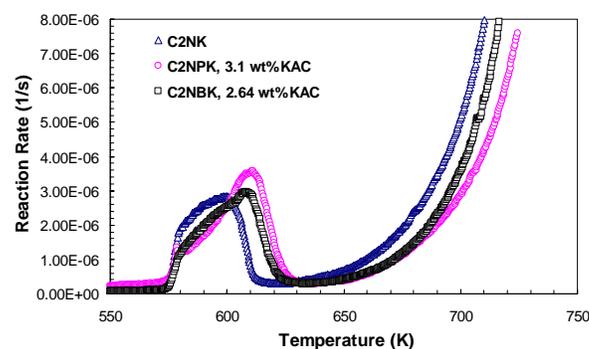
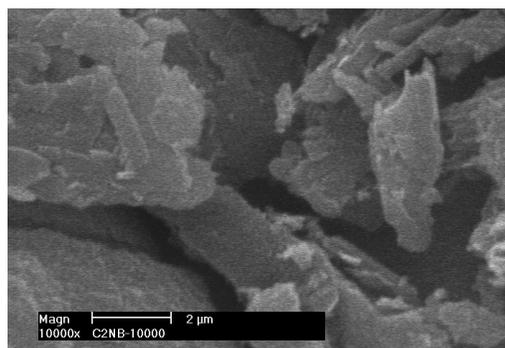*Figure 1*. TPO of sample C2N in the presence of catalysts.
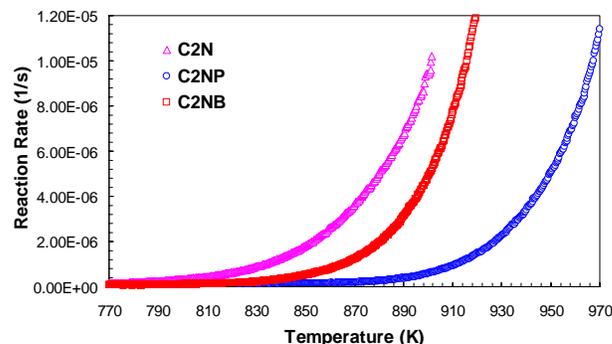
Figure 2. TPO of C2N sample doped with P or B.
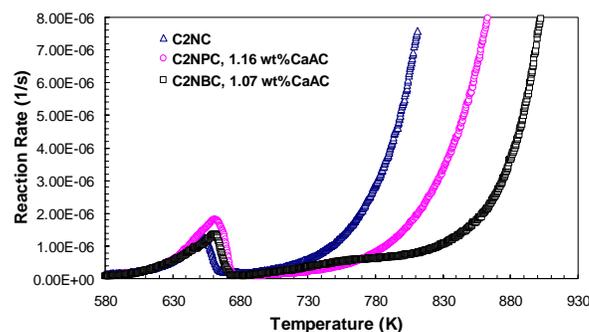
Figure 3. TPO of inhibitor-doped samples in the presence of Ca.

Figure 4. TPO of inhibitor-doped samples in the presence of K.

Figure 5. Scanning electron micrograph suggesting the existence of a B_4C layer on the carbon surface.