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CHEMICAL VAPOR DEPOSITION: STABLE CARBONS FROM LOW-RANK COALS

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ABSTRACT

A chemical vapor deposition (CVD) technique has been used to increase the oxidative stability of activated carbons. Activated carbons prepared from Gascoyne lignite (North Dakota) by thermal or potassium hydroxide activations were subjected to BCl_3 in helium at 727°C with or without benzene for a limited period of time, followed by annealing in helium at 900°C for three days. Untreated and acid-washed coal samples were used to assess the magnitude of the effect of mineral matter in the coal on the boron coating. The oxidative stability of the boron-modified carbons was determined from the decomposition curves obtained from the thermogravimetric analysis.

Modification of the as-received, KOH-treated carbon yielded oxidatively stable carbons up to an initial temperature of 520°C , compared to about 350°C for the starting material. Similar results were obtained for the carbonized Gascoyne lignite. Sulfurous acid washing of the Gascoyne significantly enhanced the thermal stability (600°C) of the boron-modified carbon.

INTRODUCTION

A major limitation in the use of carbons is their oxidative instability in air at high temperatures, usually greater than 400°C . At higher temperatures, the carbon reacts with oxygen in the air to produce CO and CO_2 . Some high-surface-area carbons could be utilized as catalysts or catalyst supports or in separation technologies at higher temperatures if they could be stabilized against oxidative degradation.

The application of a protective layer on the carbon surface could block oxygen from reacting with the surface carbons, or it could inhibit the reaction of oxygen with the surface carbon. Previous work demonstrated that boron atoms substituted for carbon atoms on the surface of a carbon fiber, composite, or graphite inhibits the oxidation reaction (1). Diffusion of boron via solid contact was attempted but gave low incorporation. Recently, a CVD reaction was used to form a protective layer on carbon fibers (2). This procedure resulted in a high concentration (25%) of boron, corresponding to the formula BC_3 . A similar reaction of boron trichloride and benzene vapors on a hot activated carbon surface could form a similar boron carbide protective coating. In this paper, we report the preparation and performance of the protective layer formed in this manner on sorbent and catalytic carbons.

EXPERIMENTAL

Preparation of CVD Carbons

As-received Coal Corporation of Victoria (CCV) lignite carbon was dried at 110°C overnight. The predried carbon (1.62 g) was packed in a quartz tube. The tube was placed in a vertical furnace and attached to a gas inlet. The outlet was attached to a bubbler filled with NaOH solution to trap HCl or BCl_3 . The carbon was heated to 727°C , and vapors of BCl_3 diluted with vapors of helium saturated with benzene were passed through the carbon. The CVD was carried out for 4 hours.

In some cases, benzene was not used, and vapors of BCl_3 diluted with nitrogen were used for carbide deposition.

The vapor-deposited carbon was annealed by heating in a gentle flow of helium at 900°C for 72 hours. The annealed carbon was grayish with a silvery mirror. The weight of the annealed carbon was 1.6 g.

TGA Determinations of Stability in Air at High Temperatures

Determinations of stability in air were conducted in a Dupont Thermal Analyst 2100 system with the TGA 951 analyzer module. Samples (50 mg) were heated at a rate of $25^\circ\text{C}/\text{min}$ in an air stream.

RESULTS

Boron-Deposition on KOH-Activated Carbon

Several carbons and chars were treated to increase their stability in air or hydrogen atmospheres. Initially, the chemically activated carbon produced by the KOH method was utilized. This carbon was prepared in Australia (CCV) from Gascoyne, North Dakota, lignite by pyrolysis in KOH. The CCV carbon had a high surface area (N_2 -BET = 1325 m²/g) but was not as thermally stable as a carbon prepared by steam activation. The thermogravimetric analysis (TGA) tests in air showed that the CCV carbon began to react with air at 351°C (Table 1), and at 660°C, the carbon was completely consumed. The decomposition curve was smooth, and the derivative peak was symmetrical, indicating a consistency in the oxidation mechanism. The residue present after the TGA experiment indicated an ash content of 7.3%. Much of the residue is potassium remaining from the earlier activation procedure. It is difficult to wash out all the potassium salts, and they can be the cause of the lower stability of the CCV lignite. The potassium salts will catalyze the gasification-combustion reactions that occur as the carbon is heated in air (or another reactive atmosphere).

Chemical vapor deposition was performed by passing a helium stream containing boron trichloride and benzene vapors through the CCV carbon at 727°C for 4 hours. The carbon was further treated by annealing at 900°C in the helium stream for 72 hours. The TGA test with the resulting carbon demonstrated an increased stability; the oxidation was not initiated until 507°C and was completed at 854°C. The decomposition curve was a little less symmetrical, indicating two different types of material or mechanisms were involved in the gasification-combustion reaction with air. In this experiment, an ash representing 11.2% of the material remained after the TGA experiment was completed. Thus a substantial amount of boron had been added.

A control experiment was performed by heating the CCV carbon in a helium stream with no reagent gases at 727°C, followed by annealing at 900°C. The TGA test on this sample exhibited an initial oxidation at 381°C, and the oxidation proceeded more slowly than the oxidation of the original CCV carbon, but this was higher than the oxidation rate of the CVD carbons. The ash content was 7.2%, similar to that of untreated CCV carbon. Thus the annealing procedure appeared to increase the stability by only a small factor, probably due to removal of the more reactive carbon material.

The presumed reaction is substitution of boron on the benzene or benzene decomposition products to form a graphitic layer with substitutional boron (2). It seemed possible that boron could form a protective coating on an activated carbon in the absence of the benzene by reacting directly with the carbon surface. Thus a second CVD experiment was performed with the CCV carbon, in which a helium stream containing only the boron trichloride was passed through the heated (727°C) carbon. The carbon was annealed as before. The TGA test of the carbon produced by this method showed an initial oxidation temperature of 518°C, but the decomposition occurred more rapidly, being complete at 777°C. In this case, the ash weight was 4.4%, indicating that some of the potassium present in the carbon must have been lost. The chlorine liberated from the boron trichloride may have formed potassium chloride which devolatilized at the high temperatures.

Boron Deposition on Gascoyne Char

Several reactions were performed with a Gascoyne carbon that was produced by carbonizing a cleaned lignite under conditions similar to those used in the CVD procedure. The lignite was washed with sulfurous acid to exchange out the calcium and alkali metals associated with the carboxylate groups of the coal. The exchanged coal was carbonized at 727°C and then 900°C to produce the carbon precursor for the CVD experiments. The control experiment on the carbon from the acid-exchanged Gascoyne gave an initial oxidation temperature of 527°C. The ash content of the untreated carbon was 5.8%.

A CVD carbon was then prepared from the 900°C-annealed carbon using a helium stream containing boron trichloride and benzene vapors at 727°C. The resulting carbon was annealed at 900°C. The TGA of this CVD carbon showed a remarkable improvement in stability, with an initial oxidation temperature of 600°C and complete oxidation at 890°C (See Figure 1). The ash content of this material was 12.85%, indicating a substantial amount of boron was incorporated.

Treatment of the 900°C-annealed carbon with boron trichloride vapor in helium (no benzene) was performed at 727°C for 4 hours, followed by annealing at 900°C to give the CVD carbon. The TGA test with this CVD carbon showed an initial oxidation temperature of 522°C, similar to that obtained from the 900°C-annealed precursor carbon. The ash content obtained in this test was 8.8%, indicating that boron was incorporated, even though benzene was not added to condense with the boron.

The addition of a carbon vapor source (benzene) to the boron trichloride generated an effective protective boron carbide coating on the surface of the lignite-derived carbons. The lower stability of the CVD carbons produced by boron trichloride vapor alone compared to the carbons produced by boron trichloride-benzene CVD carbon suggests that the carbon structures are different in these two types of samples, but we do not yet understand what boron forms are present. Although aromatic volatile compounds released during carbonization of a lignite might decompose to provide the carbon needed for the boron carbide layer, the type of volatile carbon species released in the gasification of an activated carbon at 727°C (CO, CO₂, CH₄) may react with the boron differently or not at all. On the other hand, condensation of the boron and carbon species generated from decomposition of the benzene and boron trichloride gases does form a protective edge structure or layer. Boron carbide has also been deposited on carbon fibers in a high-temperature (1200°–1500°C) reaction of boron trichloride vapor with hydrogen (3).

Carbonization of an as-received Gascoyne lignite was also studied to determine whether the mineral content of the resulting carbon affects the oxidation of the carbon. For the control (non-CVD), the lignite was first carbonized at 400°C, then 727°C, and finally 900°C. The initial oxidation temperature was similar to that obtained from similar thermal activation of the acid-washed lignite discussed above. When the char produced at 400°C was treated with boron trichloride vapor in helium for 2 hours at 727°C and then annealed at 900°C, the TGA test on this CVD carbon gave an initial oxidation temperature of 503°C. Thus, the stability actually decreased as a result of the boron treatment. The ash content of this boron-CVD carbon was quite high (16.0%). It is likely that much of the ash represents reactions of the mineral matter with the BCl₃ to form calcium and sodium chloride.

When the boron trichloride vapor treatment was continued for 4 hours, the resulting CVD carbon showed an initial oxidation temperature of 516°C and final burnout at 826°C. This is still somewhat less stable than the carbons produced without boron CVD.

CONCLUSIONS

The stability of activated carbons to air oxidation was remarkably improved by CVD with boron trichloride and benzene vapors. A boron carbide layer on a lignite-derived carbon was able to increase the stability to air oxidation so that the carbon could be used in an air stream at 600°C without decomposition. A very high surface area carbon was stabilized significantly by the CVD of boron carbide.

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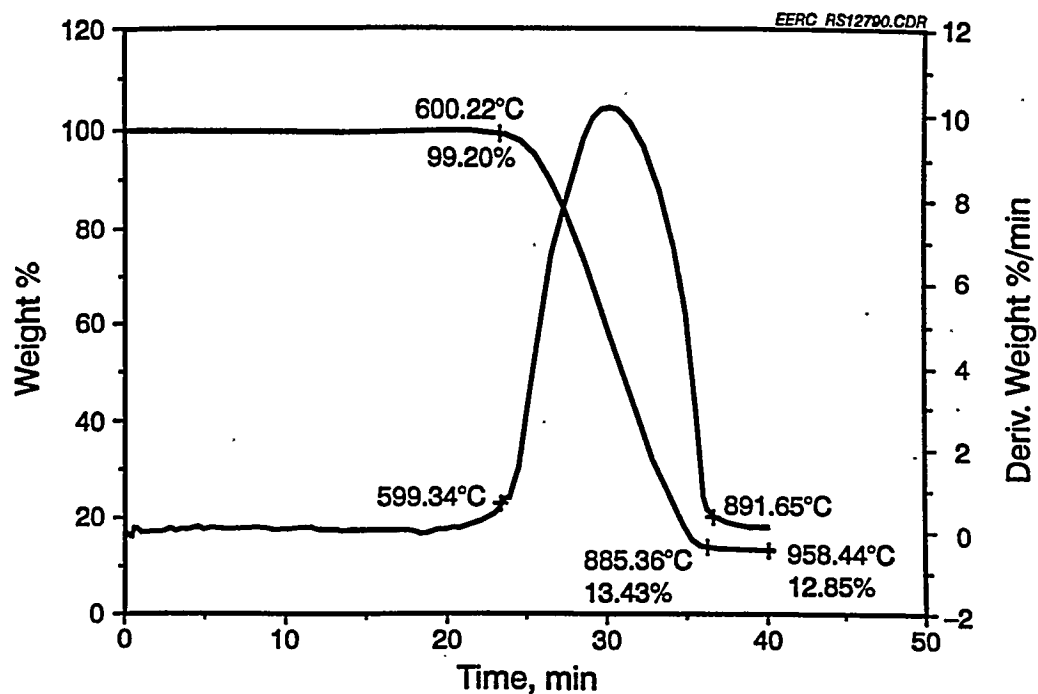


Figure 1. TGA of CVD-Gascoyne Activated Carbon

TABLE 1

Chemical Vapor Deposition on Carbons

Carbon/Char, g	CVD Method	Activation	Init. Oxid. Temp.
CCV-Lig	-	-	351
CCV-Lig	$\text{BCl}_3 + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	519
CCV-Lig	$\text{BCl}_3 + \text{benzene} + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	507
CCV-Lig	-	$727^\circ\text{C}/\text{He}/4 \text{ hr}$ $900^\circ\text{C}/\text{He}/72 \text{ hr}$	381
Gascoyne/carb. 400°C	$\text{BCl}_3 + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	516
Gascoyne/carb. 400°C	$\text{BCl}_3 + \text{He}/727^\circ\text{C}/2 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	503
Gascoyne/carb. 400°C	-	$727^\circ\text{C}/\text{He}/4 \text{ hr}$ $900^\circ\text{C}/\text{He}/72 \text{ hr}$	532
Gascoyne/carb. $400^\circ\text{C}/727^\circ\text{C}/4 \text{ hr}/$ $900^\circ\text{C}/72 \text{ hr}$	$\text{BCl}_3 + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	536
Gascoyne $\text{H}_2\text{SO}_3\text{-Cl}/\text{carb. } 400^\circ\text{C}$		$\text{He}/727^\circ\text{C}/4 \text{ hr}$ $900^\circ\text{C}/\text{He}/72 \text{ hr}$	527
Gascoyne $\text{H}_2\text{SO}_3\text{-Cl}/$ carb./4 hr/ $727^\circ\text{C}/4 \text{ hr}$ $900^\circ\text{C}/72 \text{ hr}$	$\text{BCl}_3 + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	522
Gascoyne $\text{H}_2\text{SO}_3\text{-Cl}$ carb./4 hr/ $727^\circ\text{C}/4 \text{ hr}$ $900^\circ\text{C}/72 \text{ hr}$	$\text{BCl}_3 + \text{benzene} + \text{He}/727^\circ\text{C}/4 \text{ hr}$	$900^\circ\text{C}/\text{He}/72 \text{ hr}$	600

$\text{H}_2\text{SO}_3\text{-Cl} = \text{H}_2\text{SO}_3 - \text{Cleaned}$