

CATALYTIC ACTIVITY OF CARBON ENRICHED FLY ASH

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Introduction

As summarized in a recent review¹, carbon materials exhibit various degree of catalytic activity in reaction such as dehalogenation, hydrodehalogenation, hydrocracking of alkyl aromatic hydrocarbon, oxidation, and destructive oxidation of halogenated compounds. Some of these catalytic reactions are of environmental interest and could be used to dispose of waste materials. Under these conditions, cheap, disposable catalytic carbon materials could be useful.

Over 340 million tons of fly ash is generated each year, worldwide². In the United States, the quantity is about 50 million tons/year. Until recently, the carbon content of the fly ash was in the range of 3-5%. However, with the development of low NO_x burners, the carbon content of the fly ash has risen to 10-15%. This high carbon content precludes the traditional use of fly ash in cement manufacturing and transforming the material from a by-product to a waste. If this fly ash could be fractionated into a low carbon (< 5% C) fraction to be used for cement production and a carbon-enriched (50-80% C) fraction to be used as an absorbent or catalyst, then there would be a significant economic advantage.

Several uses have been considered for the carbon-rich fraction, including application as cheap active carbons for waste water purification and as a sorbent for gas cleaning. We found that the carbon in the carbon-enriched fractions obtained by several methods of fractionation could be used as a low cost, active catalyst for the hydrodehalogenation of halogenated condensed polyaromatic hydrocarbons.

Experimental

The fly ash used in this study was generated from a low sulfur (< 2%) bituminous coal burned in a pulverized coal combustion power plant, Colbert, of TVA. This fly ash has a 10.4% C content and a surface area of 13 m²/g.

The fly ash was separated into a carbon-rich and an ash-rich fraction by triboelectrostatic (TE) separation³ and/or pentane agglomeration by multiple step fractionation. For example, the carbon-enriched fraction in Table 1 was obtained by repeating the triboelectrostatic method three times, followed by the pentane agglomeration method. The pentane agglomeration procedure was done as follows: ground

Colbert fly ash (1.5 g.) was added to 10 ml. of pentane. This solution was stirred for half an hour, after which 30 ml. of distilled water was added. The carbon that floated to the top was recovered, and dried under vacuum at 100 °C. The carbon content was determined by TGA.

The activity of the catalysts was measured by performing micro tests in sealed 7 mm o.d. heavy walled glass tubes⁴, in the presence of hydrogen donors, followed by analysis of the reaction products by gas chromatography. The specific reaction conditions are given in Tables 1 and 2. Details of the catalyst activity test were previously discussed^{4,5}.

Results and Discussion

Various carbon materials, for example carbon blacks, are active catalysts in hydrodehalogenation reactions of halogenated condensed aromatic compounds⁵ and/or hydrocracking reactions⁴ of condensed aromatic compounds. We have tested several high carbon fly ashes and carbon-enriched fractions for their catalytic hydrodehalogenation and hydrocracking activity. None of the fly ash materials are active catalysts in hydrocracking reactions, but all of them are in various degree active in hydrodehalogenation reactions. The results for the catalytic activity of a carbon -enriched fly ash in several hydrodehalogenation reactions are presented in Table 1.

The method used for the carbon enrichment of the fly ash has an important effect upon the catalytic activity of the carbon-rich fraction. To illustrate this point we tested the catalytic activity of several fly ash fractions obtained from Colbert fly ash in the hydrodehalogenation reaction of 1-bromo-naphthalene (Table 2). For reference, we presented also the catalytic activity of Cabot BP2000 carbon black. We found that while a continuous TE separation increases the carbon content of the carbon-enriched fractions, the catalytic activity does not increase significantly. Scanning electron microscopy of the samples indicate that while the sample contains more carbon, the surface of the carbon particle is covered by a fine layer of mineral matter. Further separation of the carbon-rich sample by pentane agglomeration cleans the surface and increases substantially the catalytic activity from 26% to 65%. Direct pentane agglomeration is less effective, as data in Table 2 illustrate. This catalytic activity appears to increase with increasing carbon concentration in separated fractions and further appears

to depend on the nature of the separation itself.

Our preliminary data indicate that carbon-enriched fly ash fractions could be a source of inexpensive catalysts for environmentally relevant reactions. The study continues to determine to find the best method to obtain active carbon surfaces after enrichment. The separation of a valuable, relatively small fraction from high carbon fly ash will leave a large fraction of low carbon material for the use in the cement industry.

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Table 1 Catalytic activity of carbon-enriched Colbert fly ash*

Substrate	Catalyst	H-donor	Temp. (°C)	% Dehalogenation
1-Cl-naphthalene	No	9,10-DHP	410	8
	Yes			23
1-Br-naphthalene	No	9,10-DHP	350	0
	Yes			71
9-Br-phenanthrene	No	tetralin	350	2
	Yes			70

* 43% C with a surface area of 50 m²/g.

Reaction Conditions :wt. ratio catalyst:substrate:hydrogen donor 1:2.5:10, for 1h.

9,10-DHP = 9,10-dihydrophenanthrene

Table 2. Carbon materials catalyzed hydrodehalogenation of 1-Br-naphthalene

Catalyst	% C in fly ash	% Dehalogenation
none	-----	0
carbon black BP2000	>97	57
Colbert Fly Ash		
as received	10.4	20
TE Fractioned		
Carbon rich	19	26
Ash rich	7	12
Multiple Step Fractionation		
Carbon rich	44	65
Ash rich	8	33
Pentane Agglomeration		
Carbon rich	34	47
Ash rich	6	26

Reaction Conditions :wt. ratio catalyst:substrate:hydrogen donor 1:2.5:10 at 350 °C for 1h.

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