

Carbon Materials - Activity and Selectivity in Hydrocracking Reactions.

M. Farcasiu, C.M. Smith, E.P. Ladner
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, Pittsburgh, PA 15236

A.P. Sylwester
Sandia National Laboratory, Albuquerque, NM 87185

Keywords: carbon materials, hydrocracking catalysts, selectivity.

INTRODUCTION

The use of carbon materials in catalytic systems has been traditionally associated with their properties as supports (1). There are, however, some literature data describing their use as catalysts. It was reported that, after activation with ammonia, some carbon blacks are good oxidation catalysts (2) and that some activated carbons are active in the cracking of hydrocarbons (3). Our data (4,5), as well as recent data by Grunewald and Drago (6), show that some carbon materials could act as catalysts for specific reactions. Thus, a high surface area carbon molecular sieve was active for oxidative dehydrogenation reactions at temperatures of about 2300C (6). We have used carbon materials with variable surface area as catalysts for C-C cleavage in a reductive medium and at temperatures above 3200C (4,5).

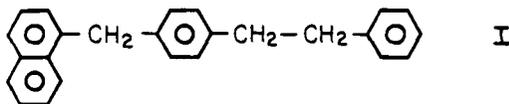
In this paper, we describe a systematic study of the catalytic activity of carbon blacks of different surface area and origin and also the catalytic activity of carbon materials obtained by the pyrolysis of polymers such as resorcinol - formaldehyde and polyacrylonitrile.

EXPERIMENTAL

Materials and Analytical Procedures. 9,10-Dihydrophenanthrene (9,10-DHP) was obtained from Aldrich Chemical Co. Black Pearls 2000, Monarch, Mogul and Regal carbon blacks were provided by Cabot Corporation; graphite powder -325 mesh was supplied by ALFA. The carbon materials from the carbonization of polyacrylonitrile and resorcinol-formaldehyde polymers were prepared at Sandia National Laboratory and their methods of preparation have been described previously (7-11). The results of the analyses performed on different carbon materials used in this work are given in Tables 1, 2, and 3.

The elemental analyses were performed by Huffman Laboratories, Golden, CO, and at the Pittsburgh Energy Technology Center. The surface area of various carbon materials was measured in Prof. D. Smith's laboratories at the University of New Mexico in Albuquerque and at Sandia for the carbon materials from the polymer pyrolyses.

4(1-Naphthylmethyl)bibenzyl, I, was prepared in Prof. Paul Dowd's laboratory at the University of Pittsburgh and completely characterized, as previously reported (5). Dichloromethane was stored over 4A molecular sieves.



Glass reaction tubes were made of Pyrex tubing, 5 x 7 mm (i.d. x o.d.). Sealed sample tubes were approximately 75 mm long.

Gas chromatographic analyses were carried out on a Hewlett Packard Model 5890 gas chromatograph equipped with an SE-30 60m capillary column. Gas chromatography/Mass spectra (GC/MS) were obtained on a Hewlett Packard GC/MS Model 5985 instrument equipped with a 30 m SE-52 capillary column.

Identification of reaction products was accomplished by GC/MS analysis and, when possible, by GC comparison with authentic samples. Reported product yields and overall conversion of I are based on capillary GC.

General Experimental Procedure. The reaction components (9,10 DHP, ca. 100 mg, I, ca. 25 mg, and catalysts) were weighed into open-ended glass reaction tubes. The tubes were flame-sealed, and no precaution was taken to exclude air. Warm water was used to melt the hydrogen donor and ensure the mixing of the reactants. The samples were placed upright in a temperature-equilibrated Lindberg muffle furnace and heated at the indicated temperatures for given times. The samples were removed from the oven, cooled to room temperature, and diluted with ca. 0.5 mL of dichloromethane. The samples were filtered through a plug of MgSO₄ and glass wool. An additional 0.5 mL of dichloromethane was used to wash the filter and, in the catalytic reaction, the carbon black catalyst. An aliquot of the resulting solution was analyzed by gas chromatography. The recovery was checked for selected experiments with an internal standard.

Catalytic Activity. As a measure of the catalytic activity, we determined: the overall conversion (thermal + catalytic), the catalytic conversion, and the selectivity of the catalytic conversion toward cleavage of the C-C bond between the naphthalenic ring and the adjacent aliphatic carbon. The selectivity of the above-described cleavage is calculated as the percent of the catalytic conversion only.

Deactivation, Recovery and Reuse of Black Pearls 2000. Black Pearls 2000 was recovered from several different reactions, washed, and dried for reuse. In a typical procedure, the catalyst was recovered from a reaction using compound I and 9,10 DHP, which had been run at 420°C for 1 h. The samples were prepared as described above in the general procedure. At the end of the reaction time, the tubes were cooled to room temperature. The reaction mixture was filtered through a filter paper and the retained catalyst was washed with dichloromethane and cyclohexane. The catalyst was washed

exhaustively until the GC analysis indicated only the presence of the solvent. The Black Pearls was dried in vacuo at 105°C for 4 h. Surface area determination and elemental analyses of the used catalyst are presented in Table 1.

RESULTS AND DISCUSSION

Soon after observing the catalytic activity of carbon blacks for the cleavage of C-C bonds, we found that not all carbon materials act as a catalyst. Therefore, we initiated a study to determine what features make some carbon materials active. Obvious candidates were chemical composition, surface area, and the structure of the carbon skeleton. As a first step of this study, we looked at several carbon materials of different origin and properties and tested their catalytic activity for reactions of compound I in presence of 9,10 dihydrophenanthrene as H-donor.

Cabot Carbon Blacks as Catalysts We used four carbon blacks (Table 1) obtained from Cabot Corp. and found that all four were active as catalysts for selective cleavage of C-C bonds. Their catalytic activity was proportional to their surface area. When the Cabot carbon blacks were present in quantities that provided equivalent surface area their catalytic activity and selectivity were very similar (Table 4). We found, however, that another commercial carbon black Norit (1300 m²/g) exhibits only about 77% of the activity of BP2000 for equivalent surface area.

For comparison, Alpha graphite does not exhibit any catalytic activity under our reaction conditions.

Carbon Materials from Carbonization of Organic Polymers A variety of carbon materials can be obtained by carbonization of organic polymers under controlled conditions (7-11). We investigated the carbonization products of polyacrylonitrile and of resorcinol-formaldehyde foams prepared at Sandia NL.

- a. **Carbonized Polyacrylonitrile Polymers (PAN) as Catalysts** Polymers pyrolyzed at various temperatures (Table 2) were tested for their hydrocracking activity (Table 5). They have substantially lower surface area and catalytic activity than the Cabot Carbon Blacks, but exhibit the same selectivity. After 1h at 422°C, the catalytic conversion of I of 1g is 1.65 %/ m² catalyst for carbon black BP2000 but only 1.1 %/ m² catalyst for PAN 410. Also, while the surface area of PAN 410 (pyrolyzed at 1200°C) is almost twice as large as that of PAN 1448 (pyrolyzed at 2000°C), the catalytic conversion of I is - four times larger with PAN 410 than with PAN 1448. Obviously, surface area is one, but not the only, factor in the activity of carbon materials.
- b. **Carbonized Resorcinol-Formaldehyde Foams (CRF) as Catalysts** A systematic study of carbon materials as catalysts was possible because carbon materials could be obtained by controlled pyrolysis of resorcinol-formaldehyde foams (9). For each pyrolysis temperature, several surface areas of carbon material could be obtained (10). The samples used in this paper are described in Table 3 and their catalytic activity is presented in Table 6. It can be seen that for materials pyrolyzed at the same temperature the activity is

proportional to the surface area, while for materials with the same surface area, the activity depends on the pyrolysis temperature (Fig.1). The CRF materials are the most active catalysts among the materials we have investigated so far. The catalytic conversion at 400°C in 1h for 1g of I is 0.54%/m² of CRF (pyrolyzed at 1050°C) and only 0.34 % /m² of BP2000.

Activity of the Reused Carbon Materials We have conducted some preliminary experiments in which carbon black BP2000 was recovered after reaction and re-used (see experimental part, Tables 1 and 7). These experiments showed that the reactivated BP2000 has an elemental composition different from the initial material and its surface area is reduced by ~30%. The catalytic activity of the recovered material is also reduced by 30%, but the selectivity remains the same.

Charge Distribution Analysis of Carbon Materials Charge Distribution Analysis (CDA) is a new method, invented by F.Freund (12), which makes possible the determination of the charge on the surface of solids as a function of temperature. Several of the carbon materials used as catalysts in this work have been studied by F.Freund by CDA. In all cases, the carbon materials that are acting as catalysts started to develop positive charges on their surface when heated in an inert gas at temperatures around 3000°C. We have shown that carbon black BP2000 becomes catalytically active for the C-C cleavage reaction at ~ 3200°C, and we have discussed possible mechanistic implications (4,5). Further work is being carried out to determine whether the selectivity of carbon materials for the cleavage of C-C bond adjacent to a condensed polyaromatic structures is related to this positive charge on the surface of the catalyst.

CONCLUSIONS

Our results show that no simple relationship exists between the catalytic activity of some carbon materials for selective cleavage of carbon-carbon bonds adjacent to condensed polyaromatic rings and the elemental composition or surface area of these materials. The activity is dependent, however, upon the precursor used to generate the carbon material. Moreover, for a given precursor the activity is determined by the method of conversion to the carbon material. It remains to be established what elements of structure are responsible for the observed activity in carbon materials that are catalytically active.

ACKNOWLEDGEMENTS

We thank R.W. Pekala of Lawrence Livermore National Laboratory for the samples of CRF materials and Dr.F. Freund from SETI-NASA for the CDA determinations.

DISCLAIMER

Reference in the paper to any specific commercial project, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. Kaminsky, M.; Yoon, K.J.; Geoffroy, G.L.; Vannice, M.A. *J.Catal.* 1985, 91, 388. Venter, J.J.; Vannice, M.A. *J.Amer. Chem. Soc.* 1989, 111, 2377 and references therein.
2. Boehm, H.P., "Structure and Reactivity of Surfaces," C.Morterra, A.Zecchina and G.Costas Editors, Elsevier Science publishers B.V., Amsterdam, 1989.
3. Greensfelder, B.S.; Voge, H.H.; Good, G.M. *Ind. and Eng. Chem.* 1949, 41, 2573.
4. Farcasiu, M.; Smith, C. *Prepr. Pap. Am.Chem.Soc.Div.Fuel Chem.* 1990, 35, 404
5. Farcasiu, M.; Smith, C. *Energy & Fuels* 1991, 5, 83.
6. Grunewald, G.C.; Drago, R.S. *J.Amer.Chem.Soc.* 1991, 113, 1636.
7. Sylwester, A.P.; Aubert, J.H.; Rand, P.B.; Arnold, C.J.; Clough R.L. *ACS PMSE Preprints* 1987, 57, 113.
8. U.S.Pat. 4,832,881 (1989).
9. Pekala, R.W. *J.Mat. Sci.* 24, 1989, 3221.
10. Pekala, R.W.; Kong, F. *ACS Polym. Preprints*, 1989, 30, 221.
11. Aubert, J.H.; Sylwester A.P. *J.Mat.Sci.* 1991 (In Press).
12. Freund, M.M.; Freund, F.; Batlo, F. *Phys Rev.Lett.* 1989, 63, 2096.

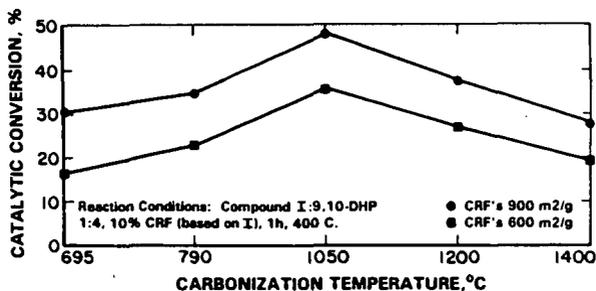


Fig.1 Influence of the Carbonization Temperature on the Catalytic Activity of CRF Carbon Materials.

Reaction conditions : I:9,10DHP 1:4 (wt), 10 % CRF (based on I), 1h, 400°C.

Table 1 Properties of Carbon Blacks form Cabot Co.

Material	Surface Area m ² /g	Dry loss %	Elemental C H		Analysis S	Dry O	Basis % Ash
Regal 400 R	86	2.3	95.9	0.5	0.9*	1.5	0.9
Mogul L	138	3.2	94.9	0.5	1.0	3.0	0.5
Monarch 1300	560	7.9	88.9	0.5	1.1	7.5	2.8
Black Pearls 2000	1475	10.9	96.1	1.4	1.4	1.4	1.2
Black Pearls 2000, recovered*	1026	0.0	96.5	1.7	0.3	0.6	0.8

* the recovery of the used BP2000 is described in the experimental section.

Table 2 Properties of Carbonized Polyacrylonitrile Polymers.

PAN #	Temperature of Carbonization C	Surface Area m ² /g	Elemental C H		Analysis wt. N	% O*
455	700	16	73.5	0.5	15.6	10.4**
662	800	17	75.4	0.2	13.4	10.0
1260	1100	22	94.3	<0.05	3.2	2.5**
410	1200	85	96.9	<0.05	1.8	0.6
1448	2000	48	>99.9	-	-	-

* O by Neutron Activation Analysis

** O by difference

Table 3 Properties of Carbonized Resorcinol-Formaldehyde Polymers.

CRF #	Temperature of Carbonization °C	Surface Area m ² /g	Elemental		Analysis, N	wt.% O*
			C	H		
654	695	900	93.69	1.45	<0.01	-4.9
626	695	700	--	--	--	-
654	790	900	94.62	0.85	0.02	-4.1
626	790	700	--	--	--	-
1029	1050	900	94.22	0.59	0.20	-5.0
613	1050	600	92.33	0.63	0.18	-6.9
654	1200	900	97.57	0.19	0.21	-2.0
626	1200	600	--	--	--	-
571	1400	900	98.88	0.30	0.06	-0.8
624	1400	600	--	--	--	-

* Oxygen by difference

Table 4 Experiments with Various Cabot Carbon Blacks at Equivalent Surface Area of Catalyst per gram of Compound I.
In all cases 1:4 ratio (wt) Compound I : 9,10 DHP, 1h.

Carbon Black	Cat. conc. m ² cat/g I	Temp. C	overall conv. %	catalytic conv. %	selectivity %
None	-	407	5	-	(43)*
Regal	15.6	407	15.3	10.3	100
Mogul	15.6	407	15.4	10.4	97
Monarch	15.6	407	13.5	8.5	100
BP2000	15.6	407	13.6	8.6	100
None	-	428	26	-	(40)*
Regal	14	428	42	16	100
Mogul	14	428	45	19	100
Monarch	14	428	35	9	100
BP2000	14	428	46	20	100

* The selectivity of the thermal reaction is expressed as a percent of the C-C bond cleavage of the bond adjacent to the naphthalene ring vs overall conversion.

Table 5. Catalytic Properties of Carbonized PAN Polymers.

Reaction conditions: Compound I:9,10 DHP = 1:3 (by wt), 1h, 420°C.
 Different PAN carbons were added to an equivalent surface area (4.25 m² catalyst/g of I).

Carbonization temp. of PAN C	Surface Area m ² /g	Overall conv. I %	Catalytic conv. I %	Catalytic Selectivity %
700	16	15.1	0	-
800	17	14.5	0	-
1100	21	20.1	3.8	> 93
1200	85	21.0	4.7	100
2000	48	17.5	1.2	> 90
Thermal		16.2		43*

* The selectivity of the thermal reaction is expressed as a percent of the C-C bond cleavage of the bond adjacent to the naphthalene ring vs. overall conversion.

Table 6. Catalytic Properties of Carbonized Resorcinol Formaldehyde Polymers.

Reaction conditions :
 I : 9,10 DHP (wt) 1:4, 10 % wt CRF material (based on I), 400°C, 1h.

Carbonization temp. of CRF C	Surface Area m ² /g	Overall conv. I %	Catalytic conv. I %	Catalytic Selectivity %
695	900	33.4	30.4	>99
790	900	37.8	34.8	100
1050	900	51.2	48.2	98
1200	900	40.6	37.8	100
1400	900	31.0	28.0	97
695	700	19.6*	16.4	>99
790	700	25.8*	22.8	100
1050	600	38.8	35.8	99
1200	600	30.0	27.0	100
1400	600	22.1	19.1	96
Thermal		3.0		43**

• the experimental values for the overall conversion for these catalysts have been reduced by the factor of 600/700 for comparison with the catalysts that have surface areas of 600 m²/g (samples carbonized at 1050, 1200 and 1400°C).

** the selectivity of the thermal reaction is expressed as a percent of the C-C bond cleavage of the bond adjacent to the naphthalene ring vs. overall conversion.

Table 7. Activity of Fresh and Recovered* BP2000

Reaction of I in presence of 9,10 DHP, 1h, 407°C 10% BP2000 (based on I)

Catalyst	Surface area m ² /g	Overall conv. %	Catalytic conv. %	Selectivity %
None	-	5	-	44**
Fresh	1475	63	58	98
Recovered*	1026	45	40	98

* for the recovery conditions see Experimental Section.

** The selectivity of the thermal reaction is expressed as a percent of the C-C bond cleavage of the bond adjacent to the naphthalene ring vs overall conversion.