

ADDING VALUE TO COAL CONVERSION'S CHAR:
A STRATEGY FOR LOWER-PRICED FUELS

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INTRODUCTION

Coal's low hydrogen to carbon ratio gives coal physical properties that are not the most desired in fuel markets. The problem is dealt with in conversion technologies designed to upgrade coal to more desirable fuels by either: 1) chemically adding hydrogen, as in liquefaction or high-BTU gasification, or 2) the production of char, as in mild gasification. The first option is neither cost-effective nor environmentally sound. Liquefaction results in the production of one mole of carbon dioxide for each mole of hydrogen needed. The result is that despite the preferred hydrogen to carbon ratio in the fuel, carbon dioxide is produced in greater quantities than it would be by simply burning the coal. The depressed market value of char is the primary drawback of coal utilization technologies exercising the second option. Making value-added, non-fuel products from char could significantly improve the economics of overall operations and result in competitively-priced premium hydrocarbon fuels. The research goal of a growing number of groups, including ours, is to produce and describe carbon products which will command higher prices than the carbon (coal) from which they were produced.

Opportunities for developing specialty chemicals and advanced materials from coals were recently reviewed (Song and Schobert, 1993). One- to four-ring aromatics from coal may be necessary to feed the rapidly growing engineering applications of aromatic polymer materials. Development of high-performance carbon materials, such as carbon fibers, graphites, and advanced adsorbents for environmental applications, is another approach for moving coal's carbon into non-fuel uses (Economy et al., 1992; Thwaites et al., 1993). Carbons suitable for methane storage are being produced (Quinn and MacDonald, 1992). Carbon molecular sieves manufactured for commercial pressure swing adsorption (PSA) systems are now competing with zeolites for air separation applications. Illinois Basin coals have been shown to be good feedstocks for making molecular sieves from coal (Lizzio and Rostam-Abadi, 1993). Europeans and Japanese are reportedly testing carbons for adsorption of radon (Kinner et al., 1993; Nakayama et al., 1993). There are biotechnology applications involving carbon as a support material (Rittmann, 1993). Commercial use of activated carbon to reduce SO_2 , NO_x , and mercury in the flue gas from waste incineration plants is well-advanced in Germany (Brueggendick and Pohl, 1993) and Japan (Tsuji and Shiraiishi, 1991). Oxidized activated char catalysts have not only the capacity to adsorb volatile organic chlorides but, when heated, they catalyze decomposition of the adsorbed chlorides (Fatemi et al., 1993).

This paper describes a portion of ongoing efforts to differentiate between types of oxidized carbon surfaces, especially those that have catalytic activity for elimination reactions, and those that have selective adsorptive properties for organics in the aqueous phase. It is motivated by the belief that identifying now the uses for high-quality carbon will stimulate future demands. Demands for non-fuel uses of coal will pull coal toward the market place rather than having to push products on reluctant buyers who may presently consider coal products inferior.

Oxidized carbon surfaces were discovered in the 1960s to be catalysts for elimination of hydrogen chloride from alkyl halides and alkylation of aromatics (Kruse and Ray, 1966; Mahan et al., 1967; Kruse, 1969). Brief exposure to air at 550-700°C was shown to activate a wide variety of carbon substrates. Heating to 950°C destroyed all catalytic activity. Amines and potassium salts modified the selectivity of these catalysts. Other workers reported later that inactive carbon surfaces could be made active for catalysis of oxidation reactions and hydrogen halide elimination

reactions by treatment with ammonia or HCN at elevated temperatures (Boehm et al., 1984). Substitution of carbon by nitrogen atoms at the edges of the carbon sheets was postulated to be responsible for the catalytic properties. Recent studies have revealed that nitrogen incorporated in activated carbons increases resistance to burn-off with CO₂ at 850°C (Mang et al., 1992). The rate of gasification did not correlate directly with the nitrogen content. Gasification rates with 5% O₂ in argon of four carbons at temperatures between 500°C and 650°C showed the rate was significantly reduced by nitrogen at 500°C. Curves describing burn-off rates became steeper for the nitrogen-enriched chars at higher temperatures. Above 570°C a carbon prepared from a mixture of sugar and glucosamine was oxidized more rapidly than the reference sample. Enrichment of nitrogen in the remaining carbon during the combustion of carbons has been seen previously (Spracklin et al., 1991).

We report our observations of differences in surface nitrogen, oxygen and sulfur for a series of carbons as determined by X-ray Photoelectron Spectroscopy (XPS). XPS has been widely applied to study the surfaces of organic materials. Surface chemistry, which is frequently determined by varying the types of functional groups, may be revealed by XPS. Different functionalities containing oxygen, nitrogen, and sulfur can be quantitatively identified by XPS. Moreover, changes in surface functionalities due to chemical modifications can also be studied.

EXPERIMENTAL

Seven samples were prepared from granular activated carbon (GAC), Filtrasorb-400 (F-400), designated herein as AR000, manufactured from a bituminous coal by the Calgon Corporation. Proximate and ultimate analyses were made with a LECO Mac-400 and a LECO CHN-600, respectively. Brunauer, Emmett, and Teller (BET) surface area, micropore volume and mesopore volume were all calculated for nitrogen adsorption isotherms obtained at 77K using a Micromeritics Nitrogen Surface Analyzer 2400 ASAP. See Table 1.

AR000 was placed in an acid washing column and washed with 10 bed volumes of 1.0 M hydrochloric acid followed by 10 bed volumes of 1.0 M nitric acid. The carbon was then rinsed with 20 bed volumes of deionized water followed by 5 bed volumes of a carbonate solution buffered at pH 6. The carbon was then rinsed with 5 bed volumes of distilled-deionized water. The acid-washed AR000 was fluidized in ultra-high-purity (UHP) N₂ at 950°C for 30 minutes to produce the sample designated FN950, from which six samples were prepared by the methods given in Table 2. Two additional samples, SA10-14 and OSA10-14, described previously (Kruse et al., 1992), were made from a mixture of Illinois No. 5 and No. 6 coals. The oxidized steam-activated char (OSA10-14) was active as a dehydrochlorination catalyst.

Table 1. Characterization of AR000

| Proximate analysis ¹ | |
|---------------------------------|------------------------|
| Moisture | 1.1 |
| Volatile Matter | 5.4 |
| Fixed Carbon | 88.3 |
| H-T Ash | 6.2 |
| Ultimate analysis ¹ | |
| Hydrogen | 0.25 |
| Carbon | 91.80 |
| Nitrogen | 0.72 |
| Oxygen | 0.40 |
| Sulfur | 0.59 |
| BET Surface Area ² | 1035 m ² /g |
| Micropore Volume ² | 0.421 cc/g |
| Mesopore Volume ² | 0.231 cc/g |

¹ moisture-free basis

² moisture ash-free basis

XPS involves irradiation of a sample with monoenergetic x-rays resulting in subsequent emission of photoelectrons. By determining the kinetic energies of the emitted electrons, the characteristic binding energies that are dependent on the local chemical environment can be calculated. Since the escape depth is 30-60 Å, XPS is a surface sensitive technique. Functional groups and the binding energies (eV) associated with them are: elemental and organic sulfur species at 164.2±0.2, sulfates and sulfonates at 168.3±0.3, amines and pyridines at 398±0.3, pyrolic nitrogen, amides and amino groups at 400.2±0.3, ammonium derivatives at 401.2±0.3, nitrates at 405.9±0.7, metal oxides at 529.5±0.2 and 531.5±0.2, numerous special carbon-oxygen species and superoxide (O₂⁻ ions) at 533.2±0.2. Surface compositions (% atomic) calculated from XPS analyses for atoms appearing in amounts greater than 0.1% are given in Table 2 and the binding energies of selected atoms in this same group in Table 3.

DISCUSSION OF RESULTS

The adsorption characteristics of the carbons described herein were reported earlier this year (Feizoulof et al., 1993). It was found that the adsorptive capacity for p-nitrophenol increased as oxygen-containing functional groups put onto the carbon by nitric acid oxidation were removed by temperature programmed desorption.

The variation in carbon's fraction of atoms on the surfaces of the samples (see Table 2) is related to coverage by oxygen for the first eight samples and to ash-forming constituents in the last two.

Among the distribution of C 1s binding energies, it appears that the sample OSA10-14, the catalyst, has the highest fraction of carbon-oxygen functional (C-O and C=O) groups. The oxygen pattern is that to be expected, except for DS950. Fluidization at 950°C with nitrogen (FN950) produced the lowest surface oxygen, stripping away some of the oxygen on the as-received carbon. Brief air oxidation at 300°C introduced some oxygen (AO305) and boiling nitric acid even more (HN100). Some of this oxygen on HN100 was in the form of nitrates. This sample's nitrogen value was higher than any other and it had a 405.9 eV XPS peak indicative of nitrates. This extra nitrogen was lost in desorption at 405 °C (DS405). Oxygen drops to the lowest values as the desorption is continued through two higher temperatures where carbon dioxide is known to be the primary gas evolved. The increase in oxygen for DS950 is believed to have occurred after the sample was cooled. The 168 eV sulfur binding peak, not seen in the DS525 or DS725, is associated with sulfates. This is additional evidence that DS950 underwent oxidation after preparation at 950°C and prior to XPS analyses. No conclusions are drawn from the distribution of O 1s binding energies; the lack of resolution of types for the last two samples, run at a different time by a different operator, are not considered significant.

The coverage by nitrogen is approximately constant ($0.67 \pm 0.15\%$), within the accuracy of the determination at this low percentage, for nine samples (excluding HN100). Binding energies for N 1s are similar, except for HN100, which has a nitrate peak, and FN950, which shows some differentiation in the 398-400 eV range not observed elsewhere. The ratio of types of nitrogen functionalities remaining after nitrates have been removed by heating to 405°C is not what one would project by simple subtraction. There may be a transformation of material initially responsible for a part of the 400.5 eV peak to new material having a 401 eV binding energy. Decomposition of amides is a possibility. Sulfur coverage is constant for the first eight samples and much higher for the two chars from high sulfur coal, as expected. The absence of sulfate in the last two samples is surprising considering how easily sulfate appears to form in the first eight, but this too may be a difference in instrument calibration by different operators.

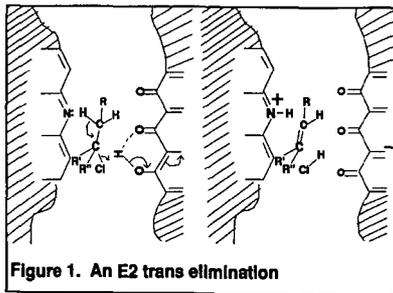
XPS binding energies at *ca.* 400 eV, usually associated with amino groups or amides, and at *ca.* 398 eV, typically associated with nitrogen bound in aromatic rings in pyridine-like fashion, were reported for three carbons having differing nitrogen contents. The peak at 398 eV was much higher with NH₂-treated carbons but neither signal was reported to be associated with catalytic activity of the carbons (Mang et al., 1992; Stohr et al., 1991). We too find no correlation between the dehydrochlorination activity of an oxidized-carbon catalyst, OSA10-14, and the surface functional groups as determined by XPS.

If nitrogen atoms contribute to the catalytic properties of oxidized carbons discovered in the 1960s, those nitrogen atoms are likely those already present in the materials. We are unaware of evidence that indicates the fixation of nitrogen in burning carbonaceous material in air at 500-700°C. If the nitrogen inhibition reported by Mang and others is spatially limited to areas adjacent to bound nitrogen atoms, the nitrogen-containing formations could be left in relief on surface areas. This effect would be most pronounced at temperatures for which the rates of gasification differ the most for nitrogen-containing structures compared to nitrogen-free zones. Depending on the dimensions of the volume affected by the nitrogen, the distribution of nitrogen atoms, and the degree of gasification, nitrogen-containing functional groups would be generated on pore wall surfaces.

It is postulated that the observed catalytic activity may be the result of specialized spatial arrangements of specific functional groups within the pores of the carbon. XPS would not reveal special spatial arrangements of two or more functional groups on pore walls which may be responsible for catalysis. Figure 1 diagrams one of many arrangements that could catalyze elimination in high yields without rearrangement of the carbon skeleton. This lack of rearrangement was of special importance to the industrial research goals in the 1960s because biodegradability of commercial detergents depended on preserving the linearity of the olefins.

CONCLUSIONS

Failure to correlate surface functional groups, identified by XPS, with catalyst activity is not unexpected if activity is dependent on functional groups located on critically-spaced opposing surfaces of pores. If catalyst sites are internal,



determining adsorption differences and increased strengths of adsorption due to chelation between properly spaced groups may be more fruitful. The use of Mossbauer Spectroscopy to follow field effects of the type studied with tin is another possibility (Larsen et al., 1982). Future work should include monitoring the evolution of nitrogen oxides in TPD analyses in addition to CO₂ and CO to determine what combination of groups may be involved.

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REFERENCES

- Boehm, H. P., G. Mair, T. Stoehr, A.R. De Rincon, B. Tereczki 1984 Carbon as a catalyst in oxidation reactions and hydrogen halide elimination reactions *Fuel* 63 (8) 1061-3.
- Brueggendick, H., F.G. Pohl 1993 Operating experience with Steag's activated carbon processes-*a/chTM*. in European waste incineration plants *Brochure published by Steag AG, Huysenalle 88, D-45128 Essen, Germany.*
- Economy, J., K. Foster, A. Andreopoulos, H. Jung 1992 Tailoring carbon fibers for adsorbing volatiles *Chemtech* October 597-603.
- Fatemi, S.M., C.W. Kruse, R.T. Lagman 1993 Oxidized activated char as an adsorbent and catalyst *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo June 13-18* 505-506.
- Feizoulof, C., V.L. Snoeyink, C.W. Kruse 1993 The effect of carbon surface chemistry on enhanced adsorption of a targeted compound from water *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo, June 13-18* 367-368.
- Kinner, N.E., J.P. Malley, J.A. Cement, K.R. Fox 1993 Using POE techniques to remove radon *Journal-American-Water-Works-Association* 85 (6) 75-86.
- Kruse, C.W., G.C. Ray 1966 Dehydrohalogenation of hydrocarbon halides *US Patent 3,240,834* Mar. 15.
- Kruse, C.W. 1969 Polymerization *US Patent 3,437,695* April 8.
- Kruse, C.W., M.I.M. Chou, C. Feizoulof, M. Fatemi, P. Beaulieu 1992 Oxidized coal char as a catalyst: characterization *Preprints of Papers Presented at San Francisco, CA ACS Div. of Fuel Chemistry, April 5-10* 37 (2) 556-563.
- Larsen, J.W., P.A. Nadar, M. Mohammidi, P.A. Montano, P.A. 1989 Spatial distribution of oxygen in coals. Development of a tin labelling reaction and Mossbauer studies *Fuel* 61 (10) 889-893.
- Lizzio, A.A., M. Rostam-Abadi 1993 Production of carbon molecular sieves from Illinois coal *Fuel Processing Technology* 34 97-122.
- Mahan J.E., R.E. Reusser, C.W. Kruse 1967 Dehydrohalogenation process *US 3,352,935*, November 14.
- Mang, D., H.P. Boehm, K. Stanczyk and H. Marsh 1992 Inhibiting effect of incorporated nitrogen on the oxidation of microcrystalline carbons *Carbon* 30 (3) 391-398.
- Nakayama, Y., H. Nagao, M. Mimura, H. Yamasita, E. Tanaka, K. Hosokawa 1993 Radon adsorption in activated carbon related to specific surface area and water absorbing *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo, June 13-18* 402-403.
- Quinn, D.F., J.A. MacDonald 1992 Natural gas storage *Carbon* 30 1097-1103.
- Rittmann, B.E. 1993 The significance of biofilms in porous media *Water Resources Research* 29 2195-2202.
- Song, C., H.H. Schobert 1993 Opportunities for developing specialty chemicals and advanced materials from coals *Fuel Processing Technology* 34 157-196.
- Spracklin, C.J., K.M. Thomas, H. Marsh, I.A.S. Edwards 1991 Nitrogen functionality in carbons and its release as NO_x during gasification *Abstracts of papers at 20th Biennial Conference on Carbon, Santa Barbara, California* 212-213.
- Stohr, B., H.P. Boehm, R. Schlogl 1991 Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate *Carbon* 29 707.
- Thwaites, M.W., M.L. Stewart, B.E. McNeese, M.B. Summer 1993 Synthesis and characterization of activated pitch-based carbon fibers *Fuel Processing Technology* 34 137-145.
- Tsuji, K., I. Shiraishi 1991 Mitsui-BF dry desulfurization and denitrification process using activated coke in *Proceedings of the EPRI SO₂ Control Symposium, Washington D.C.* 307-324.

Table 2 Surface composition (% atomic) by XPS

| ID # | Description | C | O | N | S | Si |
|-----------------------|---|------|------|-----|-----|-----|
| AR000 | Calgon F400 commercial activated carbon | 88.8 | 9.7 | 0.6 | 0.2 | 0.5 |
| FN950 | Acid-washed AR000 fluidized in high purity N ₂ at 1223 K for 30 min. | 90.8 | 7.2 | 0.8 | 0.2 | 0.4 |
| AO305 | FN950 oxidized, 573 K, 10% O ₂ /90% N ₂ , 5 min | 90.5 | 8.1 | 0.7 | 0.2 | 0.4 |
| HN100 | FN950 oxidized with 1.0 M HNO ₃ | 87.7 | 10.1 | 1.1 | 0.2 | 0.5 |
| DS405 | HN100 outgassed at 678 K in high purity N ₂ | 88.1 | 10.3 | 0.7 | 0.2 | 0.4 |
| DS525 | HN100 outgassed at 798 K in high purity N ₂ | 91.1 | 7.4 | 0.5 | 0.2 | 0.5 |
| DS725 | HN100 outgassed at 998 K in high purity N ₂ | 90.6 | 7.7 | 0.7 | 0.2 | 0.5 |
| DS950 | HN100 outgassed at 1223 K in high purity N ₂ | 87.8 | 10.4 | 0.7 | 0.3 | 0.5 |
| SA10-14 ¹ | Steam-activated, Illinois coal char ² , 1123 F 50% steam/50% nitrogen | 80.0 | 10.4 | 0.5 | 3.7 | 2.6 |
| OSA10-14 ¹ | SA10-14 Oxidized at 723 K, 10% O ₂ /90% N ₂ , 15 min | 80.0 | 10.2 | 0.8 | 3.9 | 2.3 |

¹ Al 1.6%, Fe 0.8%, Ca 0.3%.² A mixture of Illinois No 6 and No 5 coals charred at 500 °C

Table 3. Binding Energies (eV) from XPS Analyses of the Original and Treated Calgon F-400 Activated Carbon Samples

| Sample ID | C 1s % | O 1s % | N 1s % | S 2p % |
|-----------|----------|-----------|----------|-----------|
| AR000 | 284.6 62 | 531.5 52 | 399.4 27 | 164.4 71 |
| | 286.0 21 | 533.3 48 | 401.4 73 | 168.6 29 |
| | 288.9 17 | | | |
| FN950 | 284.6 62 | 531.5 32 | 397.9 11 | 164.2 61 |
| | 286.0 22 | 533.2 68 | 399.8 51 | 168.6 39 |
| | 288.9 16 | | 401.3 38 | |
| AO305 | 284.6 66 | 531.5 32 | 399.3 35 | 164.2 77 |
| | 286.1 19 | 533.2 68 | 401.2 65 | 168.6 23 |
| | 289.2 15 | | | |
| HN100 | 284.6 68 | 531.5 53 | 400.5 85 | 164.2 63 |
| | 286.2 18 | 533.2 47 | 405.9 15 | 168.4 37 |
| | 289.1 14 | | | |
| DS405 | 284.6 58 | 531.6 32 | 399.3 31 | 164.1 84 |
| | 286.0 25 | 533.1 68 | 400.9 69 | 168.2 16 |
| | 288.7 17 | | | |
| DS525 | 284.6 66 | 529.5 22 | 398.8 35 | 164.1 100 |
| | 286.1 22 | 531.5 35 | 401.1 65 | |
| | 289.6 12 | 533.2 43 | | |
| DS725 | 284.6 63 | 531.4 54 | 398.8 33 | 164.2 100 |
| | 286.0 21 | 533.3 46 | 401.2 67 | |
| | 289.2 16 | | | |
| DS950 | 284.6 65 | 531.5 55 | 400.8 31 | 164.3 83 |
| | 286.0 21 | 533.3 45 | 401.2 69 | 168.3 17 |
| | 289.3 14 | | | |
| SA10-14 | 284.6 64 | 533.2 100 | 398.6 22 | 163.9 100 |
| | 286.3 23 | | 401.2 78 | |
| | 289.7 12 | | | |
| OSA10-14 | 284.6 60 | 533.2 100 | 398.7 22 | 163.9 100 |
| | 286.0 30 | | 402.3 78 | |
| | 290.0 10 | | | |