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A NOVEL APPROACH TO HIGHLY DISPERSING CATALYTIC MATERIALS IN COAL FOR GASIFICATION

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ABSTRACT

The objectives of this project were to investigate the effects of coal surface charge on the uptake of aqueous soluble metal catalysts from solution and to determine the influence of the interfacial interaction on char reactivity. Another goal is to assess the potential of using potassium carbonate, potassium acetate or their mixtures as catalysts for char gasification. The lower cost and the high catalytic activity of the latter compound will produce economic benefits by reducing the amount of potassium carbonate required for efficient char reactivities on a commercial scale.

For the first time, the influence of measured coal surface charge on the adsorption of calcium or potassium from aqueous solution prior to gasification has been investigated. The electrokinetic properties of a North Dakota lignite, Montana subbituminous coal and Illinois No. 6 bituminous coal particles and their demineralized derivatives were measured as a function of pH. Compared to the original coals, demineralization generally increased the net negative surface charge densities on the coals. Calcium or potassium adsorption (by ion-exchange) onto the coals was strongly dependent on the pH and the surface charge on the coal particles. Metals uptake was very low (0.1-0.4 % wt.) in strongly acidic media (~pH 1) but increased dramatically as the net negative charge on the coal was increased by increasing the pHs of the coal slurries to pH 6 or 10.

To minimize the interference of the coals' inherent inorganic materials with the added calcium or potassium, the gasification studies were restricted to the demineralized coals. In a manner

similar to the effect of pH on the surface electrochemistry of the coals, the reactivities of the calcium- or potassium-loaded chars in carbon dioxide at 800°C were dependent upon the pH at which the catalysts were ion-exchanged onto the coals. For the calcium-containing chars, the reactivities increased in the order: pH 6 > pH 10 > pH 1. In contrast, the variation of the gasification rates with potassium loading pH was: pH 6 ~ pH 10 >> pH 1. However, simultaneous adsorption of the metals at ~pH 1 enhanced char reactivity relative to metals loading at pH 6 or 10. These findings are attributed to the differences in the extent of electrostatic interaction between the calcium or potassium ions and the charged coal surface during catalyst loading from solution.

This study has shown that the efficiency of metal adsorption from solution and char reactivity can be enhanced by judicious control of the surface charge properties of coal during catalyst impregnation. Thus, the goals of this project have been achieved. The publications resulting from the study are listed in Chapter 5 of this report.

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CHAPTER 1

INTRODUCTION AND STATEMENT OF THE PROBLEM

1.1 Introduction

From approximately Civil War times (1861) until World War Two (1945), coal was the dominant energy source behind U.S. industrial expansion. However, the greater convenience of low-cost petroleum resulted in a decrease in the use of coal for U.S. energy requirements after World War Two. Production fell by about one-third, reaching a low of approximately 400 million tons in 1958. Production in 1990 was 943.2 million tons.¹ With diminishing petroleum reserves, increasing uncertainty about the overall safety of nuclear power, the lack of readily available alternative sources of energy, and the increased research efforts to minimize the adverse environmental effects of coal utilization, coal is likely to emerge as a significant source of energy. Coal's potential is shown by the fact that it comprises 87% of U.S. fossil fuel resources while it currently supplies only 23% of our energy.¹

"Coal" is used to describe a large range of solid fossil fuels derived from partial degradation of plants. Table 1 shows the characteristics of the major ranks of coal, differentiated largely by fixed carbon, volatile matter, moisture, ash content and heating value.¹

TABLE 1
Major Types of Coal Found in the United States¹

Type of Coal	Proximate analysis,% Weight				Heating Value(Btu/lb)
	Fixed Carbon	Volatile Matter	Moisture	Ash	
Lignite	30	28	37	5	5500-8000
Subbituminous	40	32	19	9	8000-12000
Bituminous (High-volatile)	46	44	6	4	11000-15000
Bituminous (Medium-volatile)	64	23	3	10	11000-15000
Bituminous (Low-volatile)	66	20	2	12	11000-15000
Anthracite	82	5	4	9	13000-16000

Chemically, coal is a complex heterogeneous material and is by no means pure carbon. Attempts to unravel the chemical structure of coal have often ignored this complexity or overlooked it in an effort to make headway in describing its structural entities. Hatcher² has tried to develop a model for the chemical composition of coalified wood by analyzing the pyrolysis products using solid state C-13 Nuclear Magnetic Resonance and Fourier Transform Infrared Spectroscopy. He has developed models for brown coal wood, lignitic wood and subbituminous coal wood as shown in Figures 1A and 1B for the latter coal woods. Hatcher² points out that the models are imprecise since the models ignore the inorganic components of

Figure 1A. Structural Model for Lignitic Coal Wood.²

Figure 1B. Structural Model for Subbituminous Coal Wood.²

coalified wood and that they should be viewed as a starting point for future precise work. Comparison of the structural models of lignitic and subbituminous coal woods shows a progressive loss of oxygen in the subbituminous coal, oxygen loss being primarily via conversion of catechol-like structures to phenol and alkyl phenols.

Coal can be converted to gaseous, liquid, or low-sulfur, low-ash solid fuels. Maximum utilization of the large domestic coal reserve will depend on the ability to understand the structure and properties of coal and the environmental impacts of using it. One area of research which has received much attention is coal gasification, the incentive being the production of gases for use as fuels or chemical feedstocks. At sufficiently high temperatures, the carbon in coal reacts with steam, carbon dioxide, oxygen, air or hydrogen, generating various gaseous products. Catalysts are required to achieve economically viable rates of coal gasification. However, the potential commercial catalysts have disadvantages such as high cost, poor dispersion, inability to recover and recycle the catalyst, and reaction of the catalysts with the inorganic constituents of coal to form catalytically inactive species.³ Hence, there is a need to develop new and efficient catalysts based on fundamental understanding of coal-catalyst interaction and the dispersion of the catalysts on coal surface.

1.2 Objectives of this Research

An important parameter that has not been previously investigated in catalyzed coal gasification is the influence of coal surface charge on the interaction and uptake of aqueous soluble catalyst precursors, although there is a consensus that interfacial phenomena are involved.

The principal objectives of this work, therefore were to:

- (1) Measure the surface charge on three different ranks of coal and their demineralized derivatives.**
- (2) Develop a technique based on coal surface charge for loading coals with catalysts to ensure high catalyst-coal contact.**
- (3) Investigate the influence of the surface charge of the coals on the adsorption and dispersion of the catalysts on the coals.**
- (4) Study relationships between surface charge, metal adsorption and coal char gasification activities.**

CHAPTER 2

SURVEY OF RELEVANT LITERATURE

2.1 Coal Gasification Catalysts

Carbons in coals and chars can be converted to gaseous products by reaction with oxygen, steam, carbon dioxide or hydrogen. Equations (1) - (4) show the reactions of the commonly used gases with carbon³:

The rates of the gasification reactions can be enhanced by the addition of catalysts. During gasification, the catalysts may be modified, but not consumed. The inherent inorganic constituents in coal may also exert catalytic effects. Haynes et al.⁴ and Wen⁵ have narrowed down the list of effective catalytic materials to alkali and alkaline earth metal salts, nickel and iron oxides. The effectiveness of a catalyst has been shown to be dependent upon the cation or the anion of the catalyst precursor.

2.2 Cation Effects

To study the role of cations in char gasification, samples of a particular carbonaceous substance are impregnated with various metal compounds to a specific cation/carbon ratio. A number of investigators⁶⁻¹² have examined iron and nickel compounds as gasification catalysts. It has been concluded that these cations generally exhibit lower gasification rates compared to alkali and

alkaline earth carbonates.¹³ Walker et al.¹⁴ have reported that calcium is the most important catalyst for gasification of chars derived from raw coals when using air, carbon dioxide and steam as the reactive gases. They have also shown that for demineralized lignite chars, potassium, calcium and sodium when added by ion-exchange, are the best catalysts, in that order. Hippo et al.¹⁵ have shown that lignite char reactivity in steam is greatly enhanced by the addition of calcium cation using calcium acetate as the precursor.

Takarada et al.¹⁶ have compared the effectiveness of potassium carbonate and hexammine nickel carbonate as catalysts in gasification. It was concluded that the catalytic effect of potassium was extremely large and almost independent of coal rank whereas the effectiveness of nickel depends on the coal type. Sams et al.¹⁷ have shown that the catalytic effect of potassium on the rate of char gasification in CO_2 increases sharply at low values of K/C atomic ratio (0.019 -0.035). As catalyst concentration is increased, the rate first remains constant at the maximum value and then decreases. The attainment of a constant reaction rate is attributed to the saturation of the coal surface sites with potassium. This decrease of reaction rate is also possibly due to the plugging of the micropores by the catalysts. Heinemann et al.¹⁸ have shown that potassium-calcium oxide mixtures are only slightly less active than potassium-nickel catalysts, but the latter catalysts are more subject to poisoning by ash components than the former.

2.3 Anion Effects

Previous studies have shown that alkali and alkaline earth metal acetates, nitrates and sulfates are less active than the metal carbonates and hydroxides but more active than the halides.¹⁹⁻²⁴ A steam atmosphere is necessary to activate KCl and NaCl on carbon. Wigmans et al.²⁵ have proposed the following steam gasification mechanism of carbon in the presence of metal catalyst, M, as represented by equations (5)-(8):

It was suggested that metal-oxygen bonds are prerequisite for char gasification. Hence, it is possible that metal halides do not possess any inherent catalytic activity for gasification.²⁶ Evidence for this conclusion has been given by Mims et al.²⁷ who converted the K₂CO₃ impregnated on amorphous carbon to KCl by reaction with HCl at 573 K. They found that the catalytic activity of K₂CO₃ was destroyed. It is therefore essential that for a gasification catalyst to be effective, it must possess an oxygen-bearing anion.

2.4 Surface Charge Formation on Coal Surfaces

Low rank coals like lignites contain surface groups such as carboxylic acids and phenolic functional groups. Figure 2 shows the predominant surface functional groups on coal.^{28,29,30}

(a) Benzoic acid derivative

(b) Phenol derivative

(c) Napthaquinone derivative

(d) Pyrone derivative

Figure 2. Predominant oxygen-containing surface functional groups on coal.

In aqueous and basic media, these acidic surface groups dissociate and the coal particles acquire net negative charges as shown in equations (9) and (10). However, in strongly acidic medium the coal particles may become positively charged through protonation of the surface functionality as shown by equations (11) and (12).^{28,29} The formation of surface charge on coal is depicted by equations (9)-(12) for carboxyl (-COOH) and hydroxyl (-OH) functional groups,

where the subscript (s) designates the coal surface.

Depending on the solution pH, coal particles may experience charge reversal. The isoelectric point (IEP) is the pH at which charge reversal occurs. For coals, the IEP occurs in the acidic range ($\text{pH} < 7$).³ The surface charge development on coal is shown in Figure 3.

Figure 3. Surface charge development on coal.³¹

At the isoelectric point (IEP), the net surface charge will be zero.³² When the slurry pH is higher than the IEP, the coal surface will preferentially adsorb cations from solution, since the coal particles acquire a net negative charge. However, for slurry pHs less than the IEP, the coal surface will acquire a net positive charge and it will

preferentially adsorb anions from solution. The surface polarization of a coal particle as a function of coal slurry pH and its isoelectric point is illustrated in Figure 4.

Figure 4. Schematic representation of the surface polarization of coal particles as a function of coal slurry pH and its isoelectric point.³³

The solution pH plays a significant role in cation adsorption onto coals. If the coal particles and the cation have opposite charges, the interaction will be attractive and adsorption will be enhanced, whereas the interaction will be repulsive and adsorption will be hindered if the adsorbent and adsorbate have similar charges. This concept has been supported by Abotsi and Scaroni.^{31,34} Hence, control and modification of the pH of catalyst impregnating solutions is crucial in order to maximize catalyst precursor adsorption onto coal and possibly enhance initial catalyst dispersion.

The determination of coal surface charge of particles in solution may be accomplished using electrophoresis, the basic principles of which are shown in Figure 5.

Figure 5. Principles of Electrophoresis.

To determine the zeta potential, which is directly related to the surface charge density, the coal-water slurry is placed in an electrophoresis chamber consisting of two electrode compartments and a connecting chamber. When a voltage is applied between the two electrodes, it produces an uniform electric field in the connecting chamber and the suspended coal particles respond by moving towards one or the other electrode. Positively charged particles migrate towards the cathode (negative electrode) and the negatively charged particles migrate towards the anode (positive electrode). The velocity of particle migration is directly proportional to the magnitude

of the particle charge density. The relationship between the particle velocity and zeta potential is shown in equation (13):

$$V = DX\xi / 4\pi\mu \quad (13)$$

where D is a constant that includes surface charge density and the dielectric constant of the medium, X is the electric field in volts/cm, ξ is the zeta potential and μ is the viscosity of the medium.³³

Since the applied electric field and the viscosity of the medium are constants, the zeta potential is directly related to the velocity of the particle.

2.5 Coal-Catalyst Interaction

The reaction of gases with carbon studied under a microscope have shown that the regions of enhanced reaction rate are the interface between the carbon and the added catalyst particles.^{35,36,37} Thus, catalyst activity may be increased by using catalyst impregnation techniques which enhance carbon-catalyst contact and catalyst dispersion. One of the methods of adding metal ions to substrates to achieve high catalyst dispersion is the ion-exchange technique.¹⁵ In this technique the protons on coal are displaced by the metal ions. Such an exchange occurs in nature when ground water saturated with calcium, potassium, sodium or magnesium ions percolate through coal beds.³

When C-13 labelled K_2CO_3 was heated with char to about 800K, the CO_2 evolved was found to be C-13 labelled and it was produced exclusively and quantitatively from the decomposition of the carbonate.^{27,38} The evolution and measurement of CO_2 was monitored by TPR/QMS (Temperature Programmed

Reaction/Quadrupole Mass Spectrometry). This suggests an interaction between K_2CO_3 and carbon. Hashimoto et al.³⁹ found that the steam gasification rate of carbon impregnated with alkali metal salts was proportional to the molar amount of oxygen measured on the carbon surface. They found that KOH/carbon and K_2SO_4 /carbon chars showed strong infrared peaks at 1400 cm^{-1} and 1650 cm^{-1} . Yuh et al.²³ have attributed these peaks to K-O-C bonds, and hence it was concluded that oxygen is trapped by the metal (M) in the form of an M-O-C bond on the carbon surface. With the help of electron spin resonance (ESR) measurements, Sancier^{40,41} and Wood et al.²⁴ have found that an irreversible increase in the line width of the resonance due to free radicals (carbon atoms or group of atoms with an unpaired valence electron) in carbon black occurs when mixtures of carbon black and certain salts (K_2CO_3 or $CaCO_3$) are heated in helium to about 600 K. The line broadening was attributed to an interaction of the unpaired electrons of the free radicals with electric fields associated with metal cations of the salts. The irreversible increase in line width was demonstrated by cooling the mixtures. Cooling did not produce any decrease in line width. They suggested that this was a strong indication of an interaction between the catalyst and the carbon.

Summarizing the results of many studies by various investigators, it can be said that effective coal/char gasification catalysts are ionic salts with oxygen-bearing anions. It is also clear from these studies that the cations of the salt react with the carbonaceous material to form a chemically and thermodynamically

distinct active species that mediates the gasification process. It is generally agreed that the catalyst supplies oxygen to the carbon.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 Approach

In order to investigate the effects of coal surface oxygen functionality on coal surface charge, metal ion adsorption and gasification activity, lignite (PSOC 1482), subbituminous (PSOC 1485), and bituminous (PSOC 1493) coals were selected for this study. The selection is based on the differences in the oxygen content of the coals, which is anticipated to produce different surface charge densities and metal ion adsorption. Table 2 shows the properties of the coals used in this work. The research approach for this work is summarized as follows:

- (1) The raw coals were demineralized in a mixture of concentrated hydrofluoric acid and concentrated nitric acid.
- (2) The (surface charge densities) zeta potentials were measured for the raw coals and their demineralized derivatives as a function of the pHs of the coal-water slurries.
- (3) The adsorption of calcium or potassium ions on the raw coals and their demineralized samples were carried out as a function of the pHs of the coal slurries containing the metal ions.
- (4) Chars were prepared from the raw coals, their demineralized derivatives and catalyst containing coals. Char reactivities in carbon dioxide were studied using a Dupont 951 thermogravimetric analyzer.
- (5) The raw, the demineralized, and the metal-containing coals were studied using a variety of analytical techniques including

Atomic Absorption Spectrophotometry, X-Ray Diffraction
Analysis, Scanning Electron Microscopy, X-Ray Fluorescence,
and Surface Area Analysis.

TABLE 2
Properties of the Coals Used

Penn State Sample Number	PSOC 1482	PSOC 1485	PSOC1493
Seam	Hagel	Rosebud	Illinois#6
State	N. Dakota	Montana	Illinois
Rank	Lignite	Subbit. B	Bit. hvc
Ultimate Analysis (daf, %wt.)			
Carbon	71.34	75.78	78.07
Hydrogen	4.5	5.30	4.92
Nitrogen	1.14	1.19	1.50
Total Sulfur	0.79	0.99	5.87
Oxygen (by difference)	22.24	16.75	9.64
Proximate Analysis (As Received, %wt.)			
Moisture	34.45	25.37	9.43
Volatile Matter	28.18	27.43	34.34
Fixed Carbon	31.80	38.67	42.50
Ash	5.57	8.54	13.74

3.2 Demineralization of the Coals

Portions of the raw coals [the lignite (PSOC 1482), subbituminous (PSOC 1485) and bituminous (PSOC 1493) coals] were demineralized separately with a mixture of 1:1 concentrated hydrofluoric acid and nitric acid for 2 weeks. The volumes of acid added to each coal was such that the raw coals were completely submerged in the acid media. The demineralization was carried out in one liter Nalgene high density polyethylene bottles. Glass containers were avoided to prevent the leaching of silicates from the glass by hydrofluoric acid. The coals were then filtered through a Buchner Funnel and washed repeatedly with distilled water until the pH of the filtrate was close to pH 6 and the filtrate was virtually colorless. The demineralized coals were then dried in a vacuum oven at 343 K for two hours.

The purpose of the demineralization of the coals is to eliminate the interference of inherent metal ions with the potassium and calcium ions which will be added to the coals. Acid leaching:

(a) converts the carboxylates or carboxylic salts to carboxylic acid surface groups by exchanging the metals with hydrogen,¹⁵ (b) removes mineral oxides such as silicates and aluminosilicates,¹⁵ (c) increases the carboxyl content of coals prior to exchanging K^+ or Ca^{+2} ions with the hydrogen ions on the carboxyl groups.⁴²

Hence, demineralized coals provide a reference background for fundamental and comparative studies.

3.3 Zeta Potential Measurements

Three hundred milligrams (300 mg) of the lignite, the demineralized lignite (Dem 1482), the subbituminous, the demineralized subbituminous (Dem 1485), the bituminous, and the demineralized bituminous (Dem 1493) were separately weighed. Coal-water slurries were prepared by dispersing the weighed sample of each coal in one liter of deionized water containing 10^{-3}M AgNO_3 (0.1699 g of AgNO_3 /liter of solution) for controlling the ionic strength of the solution. High dispersion of the coal particles was achieved by vibrating in a "Branson 2200 " ultrasonic bath for 20 minutes. The suspended particles were separated from the sediments by decantation and used for the zeta potential studies.

The coal-water slurry was divided into 50.0 ml portions in 250 ml stoppered conical flasks. The pH of each 50.0 ml portion was adjusted to an initial pH value in the pH range of about pH 1 to pH 12 by dropwise addition of concentrated, 50%(aqueous by volume) or 20%(aqueous by volume) hydrochloric acid and/or ammonium hydroxide. All pH measurements were done with the aid of a "Fisher Scientific Accumet 910 pH Meter" which had been standardized at pH 4, 7 or 10. Based on preliminary experiments the samples were equilibrated for four hours by mechanical agitation using a "Burrel Wrist Action Shaker". After equilibration, the equilibrium pH value of each sample was recorded. Each sample was then transferred to the Zetameter and the zeta potentials of the coal particles were measured at room temperature using a "Pen Kem Model 501 Lazer Zee Meter".

3.4 Cation Adsorption

Calcium or potassium cation adsorption onto the raw and demineralized coal samples were studied as a function of pH using calcium acetate and potassium carbonate, respectively, as the metal sources. The initial cation concentrations used were 0.01M. In the case of coadsorption (simultaneous adsorption of calcium and potassium ions), potassium nitrate was used instead of potassium carbonate to prevent the precipitation of calcium carbonate.

The cations were loaded on the coals by the ion-exchange technique. One gram (1 gm) of each coal sample was separately dispersed in 50.0 ml of 0.01M or 0.1M of calcium or potassium solutions in stoppered conical flasks. The pH of the coal slurries were adjusted to initial pH values between 1 and 12 by addition of a few drops of nitric acid or ammonium hydroxide solutions. The coal dispersions in the metal ion solutions were then shaken for 24 hrs on a "Burrel Wrist Action Shaker", after which their equilibrium pH's were recorded. It was observed that the coal-water slurries containing metal ions at high pHs had reddish-brown color. The coal slurries were filtered and the filtrates were analyzed for calcium or potassium using a "Varian SpectrAA-20" Atomic Absorption Spectrophotometer.

Metal uptake was calculated as the differences in calcium or potassium content of the solutions prior to and after adsorption. Cation adsorption is expressed as millimoles/gram of coal. A positive calcium or potassium adsorption value indicates adsorption of the metal by the coal from the solution whereas a negative cation adsorption indicates desorption of inherent calcium or potassium of

the coal into solution and/or reduced metal ion uptake. When a net negative metal extraction from the coal occurred, the calcium or potassium concentration in the filtrate was higher than that in the initial metal solution used.

Extraction of iron from the various coals into the calcium or potassium-containing solutions were also studied as a function of pH by analysing the filtrates for iron using Atomic Absorption Spectrophotometry.

3.5 Char Gasification

Portions of the air-dried coal residues loaded with 0.05M calcium or potassium at various pHs were pyrolyzed by heating (at 293 K/min) to 1073 K in ultra high purity nitrogen (100 cm³/min) using a "Dupont 951" thermogravimetric analyzer. The temperature was held at 1073 K for 30 minutes. The nitrogen supply was then switched off and carbon dioxide was introduced at the same flow rate to initiate char gasification. Char gasification at 1073 K in carbon dioxide was conducted for about 2 hours.

3.6 Environmental Scanning Electron Microscopy (ESEM)

In order to obtain a visual image of the catalyst dispersion on the coal surface, ESEM was selected as one of the analytical techniques to study the catalyst-containing coal samples. The main difference between ESEM and traditional high vacuum scanning electron microscopy (SEM) is that the specimen chamber pressure in the former can be varied while SEM does not have this capability. Evaporation, condensation, freezing and sublimation of various

substances can be studied by ESEM by controlling the chamber pressure or specimen temperature. The greatest advantage of ESEM over traditional SEM is minimal sample preparation.

Initially 0.5 gram portions of the demineralized lignite loaded with 0.05M calcium at various pHs were crushed thoroughly using a pestle and mortar to obtain a physically homogeneous sample. The samples were then placed in the sample holder and introduced into the microscope for analysis. All ESEM (ElectroScan Corp.) scans were performed at room temperature in vacuum. The detector to specimen distance was 2mm, pressure was 5 Torr. The voltage was varied between 200-500V according to the image contrast desired. The analysis was done at Battelle Laboratories, Richland, Washington. Based on the preliminary results, ESEM analysis of the subbituminous and bituminous coal samples were not performed.

3.7 Energy-Dispersive X-ray Microanalysis (EDXRM)

Energy-Dispersive X-ray analysis is a surface analysis technique for determining elemental composition of microscopic samples. EDXRM was chosen as one of the analytical techniques in order to confirm the results of elemental analyses and Atomic Absorption Spectroscopy and to ascertain the uniformity of catalyst dispersion on the coal surface.

The instrument for EDXRM (Link Analytical) was interfaced with the ESEM. After obtaining ESEM photograph of a calcium loaded demineralized lignite particle, EDXRM was performed on selected points of interest on the same particle. Portions of the calcium loaded lignites at various pHs were also analyzed for

calcium content by EDXRM. This analysis was also done at Battelle Laboratories, Richland, Washington.

3.8 X-ray Diffraction

In order to ascertain the particle size and composition of the dispersed catalysts on the coal surface, X-ray diffraction was chosen as one of the analytical techniques to study the catalyst-containing coal samples. Samples of the demineralized lignite and subbituminous coals loaded with 0.05M calcium at various pHs were analysed at Georgia Institute of Technology, Atlanta, Georgia by using a "Rigaku Rotaflex RU-200" X-ray diffractometer. The samples were first ground into powder using a ceramic pestle and mortar. They were then spread uniformly into the aluminium sample holder cups which were supported by plexiglass. Adhesive tapes (which are transparent to X-ray) were used to hold the samples in the sample holder. The X-ray source was a Cu-K α anode. The voltage and current were maintained at 45kV and 100mA, respectively. The diffractometer was then programmed to scan diffraction angles from 10° to 50° (2 θ) at a scan rate of 0.25° (2 θ) min⁻¹. Finally the sample holder in the plexiglass housing was mounted on a slot in the path of the X-ray beam and the instrument was activated by turning on the X-ray through the computer interface.

The average crystallite size is determined from the Scherrer equation as shown by equation (14):

$$D = K\lambda / (B^2 - b^2)^{1/2} \cos\theta \quad (14)$$

where D is the average crystallite size, K is the Scherrer constant (usually K = 0.9), λ is the wavelength of the X-ray, B is the peak width

at half height, b is the instrumental broadening and θ is the diffraction angle.

3.9 Surface Area Analysis

Surface area analysis was chosen as one of the analytical techniques to study the catalyst-containing coals in order determine any correlation between surface area, catalyst loading pH and coal char gasification activity. The surface area analysis is based on the Brunauer, Emmet and Teller (BET)⁴³ equation. When a porous sorbent is exposed to a gas, initial absorption occurs as a monolayer of adsorbate. As relative pressure is increased, and the monolayer nears completion, molecules start adsorbing successively into the second and higher layers, with the result that the isotherm shows no saturation value as the relative pressure approaches unity. Equation (15) shows the mathematical form of the BET equation:

$$p/v(p_0-p) = 1/v_m C + (C-1)p/v_m C p_0 \quad (15)$$

where p is the equilibrium pressure, p_0 is the saturated liquid vapour pressure, v is the volume of adsorbate adsorbed at p/p_0 , v_m is the monolayer capacity and C is a constant. The BET equation is valid only in the relative pressure range of $p/p_0 = 0.05$ to $p/p_0 = 0.35$. Deviations below a relative pressure of 0.05 is due to neglect of surface heterogeneity, while deviations above a relative pressure of 0.35 is due to neglect of adsorbate condensation.⁴⁴

Single point BET surface area analysis was done on raw and demineralized bituminous coals loaded with 0.05M calcium and demineralized bituminous loaded with 0.05M potassium, using a "Micromeritics Flowsorb 2300" surface area analyzer. The analysis

was done at the laboratory facility of Micromeritics Instrument Corporation, Norcross, Georgia. All samples were degassed overnight before performing the surface area measurements. Adsorption was performed at a temperature of -195°C (temperature of liquid nitrogen). Krypton gas was used as adsorbate, and a Krypton cross-sectional surface area of 0.21nm^2 was used in calculating the surface areas of the coals.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Coal Demineralization

Chemical analysis of the acid leached coals shows that the ash content of the demineralized (Dem) coals, as determined by Galbraith Laboratories, Knoxville, Tennessee, is much lower than that in the unleached raw coals. Table 3 shows the percent ash content of the coals and the level of inorganic matter removal. Percent demineralization was calculated from the formula (equation 16):

$$\frac{[\% \text{ ash in raw coal}] - [\% \text{ ash in demineralized coal}]}{[\% \text{ ash in raw coal}]} * 100 \quad (16)$$

TABLE 3.

Demineralization Results

Coal	(%) Ash	% Demineralization
Raw 1482(Lignite)	5.57	
Dem 1482(Lignite)	0.92	83.5
Raw 1485 (Subbit.)	8.54	
Dem 1485 (Subbit.)	2.33	72.7
Raw 1493(Bituminous)	13.74	
Dem 1493(Bituminous)	1.38	90.0

Previous studies^{15,26} have shown that coal demineralization is achieved by the ability of hydrofluoric acid (HF) solutions to dissolve the inherent silicates and aluminosilicates while nitric acid (HNO₃) solubilizes other minerals such as iron oxides. This fact is frequently

used in acid digestion of metal species from solids prior to chemical analysis.¹⁵ In this work, Dem denotes demineralized coals.

4.2 Zeta Potential Measurements

Figures 6 and 7 show the dependence of zeta potential on pH for the raw and demineralized coals, respectively.

Figure 6. Dependence of zeta potential on pH for the raw lignite, subbituminous and bituminous coals.

Figure 7. Dependence of zeta potential on pH for Dem lignite, subbituminous and bituminous coals.

The most important feature of Figures 6 and 7 is that the negative charge density or the negative zeta potential of the coal particles increases with increase in pH. It is observed from Figure 6 that between pH 6 and 12, the raw lignite has the highest negative zeta potential followed by the raw subbituminous and the bituminous coals in that order. This trend is possibly due to the differences in the concentration of the surface oxygen functionalities and to the ash content of the raw coals. As seen from Table 2, the raw lignite has the highest oxygen content (22.24 %wt.), followed by the raw subbituminous (16.75 %wt.) and the raw bituminous (9.64 %wt.). Fushimi⁴⁵ found that the electrophoretic mobilities of coal particles were inversely proportional to their ash content. In the current work, the raw bituminous coal has the highest ash content (13.74 %wt.) but it exhibits the lowest negative zeta potential, the raw lignite has the least ash content (5.57 %wt.) but the highest negative zeta potential, while the raw subbituminous coal has an intermediate ash content (8.54 %wt.) and an intermediate negative zeta potential value. Thus it appears that the zeta potentials are mainly determined by the surface oxygenated groups on the coals. The isoelectric point (IEP) for the raw lignite, and the raw bituminous were 1.9 and 1.5, respectively. The isoelectric point is the pH at which charge reversal occurs. For the North Dakota lignite, Wen and Sun⁴⁶ found the IEP value to be pH 2.3. It is observed from Figure 7 that between pH 6 and 12, the Dem bituminous and Dem subbituminous coals have higher negative zeta potential than Dem lignite.

Comparison of the raw and the demineralized coals show that the increase in negative zeta potential with increasing pH is more

prominent in the demineralized coals than in raw coals. However, unlike the subbituminous and the bituminous coals, the demineralized lignite is less negatively charged than the raw lignite between pH 6 and 12. For the demineralized bituminous coal around pH 8.5, the negative zeta potential is more than five times (-110 mV) that of the raw coal (-20 mV). Leaching of coals in HF and HCl solutions causes the carbonyl groups on coal to be converted to carboxyl and hydroxyl groups.¹⁵ Thus the higher negative charge densities on the demineralized coals compared to those on the raw coals is due to the higher concentration and dissociation of the oxygenated surface functionalities.²⁸

The development of electrical charge on coals is based on their surface oxygen-containing weakly acidic groups (e.g. -OH , -COOH). The surface charge is mainly determined by the degree of dissociation of the weakly acidic groups.²⁸ The extent of dissociation varies widely depending upon the nature of the chemical (e.g. pH) and physical (e.g. temperature) environment of the coal. The proton is the zeta potential determining ion, since both the sign and the magnitude of the surface charge are pH dependent. At high pH values, the dissociation of the carboxyl groups are enhanced and the surface acquires a strong negative charge. The addition of acid causes the carboxyl groups to reprotonate and the surface charge becomes less negative.²⁹

4.3 Catalyst Adsorption onto the Coals

Figures 8 and 9, respectively show the results of calcium or potassium ion adsorption onto the raw coals.

Figure 8. Adsorption of calcium by the raw lignite, subbituminous and bituminous coals as a function of pH. Initial Ca^{+2} concentration was $10^{-2} \text{ mol L}^{-1}$.

Figure 9. Adsorption of potassium by the raw lignite, subbituminous and bituminous coals as a function of pH. Initial K^+ concentration was $10^{-2} \text{ mol L}^{-1}$.

From Figures 8 and 9, it is observed that in general, calcium or potassium adsorption onto the raw coals increases with increase in the equilibrium pH of the coal slurries. Previous work by Kokorotsikos et al.⁴⁷ has shown that the amount of potassium chemisorbed from potassium carbonate solution increases as the solution pH was raised. The metal ion adsorption trends correlate the negative charge densities of the coal particles which increased with increase in the pH of the coal slurries.

Calcium uptake is generally more pronounced than potassium uptake at pHs between 8 and 11. As discussed previously, the negative charge densities on the coals increase with increase in slurry pH, particularly for the lignite. Thus, the increase in metal ion adsorption at high pHs can be attributed to increased electrostatic attraction between the negative coal surface and the metal cations.

It is observed from Figure 8 that at low pHs ($\text{pH} < 5$), calcium adsorption is inhibited as indicated by the negative adsorption values. This suggests that calcium is extracted from the raw lignite and subbituminous into solution. In case of the raw bituminous coal, calcium adsorption from solution is inhibited in the entire pH range of 1 to 11. This observation may be explained by competition between calcium adsorption from solution and calcium desorption from the coal, the net result being calcium desorption from the coal into solution. A similarly behaviour is observed for potassium at pHs below 6 (see Figure 9).

Previous studies have shown that the inherent calcium in the raw coals is present in the form of calcite (CaCO_3), calcium oxide (CaO) and organically bound calcium. Unlike calcite, the organically

bound calcium is well dispersed in the raw coals and hence contributes to catalytic activity.⁴⁸ Calcite and calcium oxide are both sparingly soluble in water but quite soluble in acidic solutions. Solubility of calcite and calcium oxide in water at 25°C is 0.014 gm/L and 0.7 gm/L respectively.⁴⁹ Hence it is suggested that at low pHs (pH<5) the inherent calcium of the raw coals is solubilized and extracted into solution.

Similarly the inherent potassium in the raw coals is present in the form of potassium carbonate (K_2CO_3) and potassium oxide (K_2O). The solubility of K_2CO_3 in water at 25°C is 1120 gm/L while K_2O is very soluble in water at 25°C.⁴⁹ At pHs below 6, the coal surfaces still have some negative charge (except for those coals that have IEPs around pH 1.5 - 2.0). Hence it is suggested that potassium extraction from the raw coals is due to the solubilization of the inherent potassium and the electrostatic attraction of the negatively charged coal surface.

Figures 10 and 11 show the results of simultaneously calcium and potassium adsorption onto the Dem coals.

Figure 10. Coadsorption of calcium from solution by Dem lignite, subbituminous and bituminous coals as a function of pH. Initial $[Ca^{+2}] = [K^{+}] = 10^{-2} \text{ mol L}^{-1}$.

Figure 11. Coadsorption of potassium from solution by Dem lignite, subbituminous and bituminous coals as a function of pH. Initial $[Ca^{+2}] = [K^{+}] = 10^{-2} \text{ mol L}^{-1}$.

It is observed from Figure 10 that except for the Dem lignite, calcium adsorption increases with increase in equilibrium pH of the coal slurries. In case of the Dem lignite, maximum calcium adsorption occurs at pH 5. Above pH 5, calcium adsorption remains constant with increasing pH. It is seen from Figure 11 that for Dem bituminous coal, potassium adsorption increases with increase in the equilibrium pH of the coal slurries. However, in case of the Dem lignite and subbituminous coal, maximum potassium adsorption occurs at about pH 6. Above this pH value potassium adsorption remains steady with increasing pH. Thus in general, calcium adsorption is more prominent when calcium and potassium ions are simultaneously adsorbed onto the coals. The higher calcium adsorption may be explained by its higher valency which favours more interaction with the surface of the coals.

Figure 12 shows the result of the desorption study of iron from raw lignite subbituminous and bituminous coals as a function of pH.

Figure 12. Extraction of iron from the raw lignite, subbituminous and bituminous coals in 10^{-2} mol L^{-1} Ca^{+2} solution as function of pH.

As indicated in Figure 12 for the raw lignite, subbituminous and the bituminous coals, relatively high amounts of iron is extracted from the coals at low pHs ($\text{pH} < 3$) but the iron concentration in solution decreases to very low values at higher pHs. Previous work by Haynes et al.⁴ and Wen⁵ has shown iron oxides as one of the effective catalytic materials for coal gasification. On the basis of the data presented in Figure 12, iron loading from acidic solutions ($\text{pH} < 3$), should result in reduced gasification rates due to the inability of the coals to effectively adsorb iron in strongly acidic media. At high pHs, iron is precipitated as the hydroxides⁴⁹ and the metal may not be deposited inside the porous structure of the coal. The precipitated iron particles will very likely result in less dispersion and show less catalytic activity.

It was observed that at high pHs the coal-water slurries were reddish brown in color. The reddish brown color has been attributed to iron-humic acid complexes.⁵⁰ It has been reported that iron-humic acid complex formation increases with increasing pH.⁵⁰ Humic acid formation is reported to occur in coal during the early stages of coalification.⁵⁰

In order to investigate the effects of initial metal ion concentration on calcium or potassium adsorption, initial metal concentrations were changed from 0.01M to 0.05M. The metal uptakes, as determined by Galbraith Laboratories, Knoxville, Tennessee, are shown in Table 4.

TABLE 4

Dependence of calcium or potassium adsorption on catalyst loading pH

Demineralized Coal	Calcium (% wt.)			Potassium (% wt.)		
	pH 1±0.4	pH 6±0.6	pH 10±0.9	pH 1±0.2	pH 6±0.6	pH 10±0.2
Lignite	0.3	4.3	7.2	0.4	2.0	2.1
Subbituminous	0.2	2.9	7.8	0.2	1.9	2.6
Bituminous	0.1	3.3	5.9	0.2	3.5	2.3

The cation adsorption data shown in Figures 8 and 9 were obtained using initial cation concentrations of 0.01M Ca^{+2} or 0.01M K^{+} . These results (Figures 8 and 9) were obtained using atomic absorption spectrophotometry. The elemental analysis results in Table 4 were based on initial cation concentrations of 0.05M Ca^{+2} or 0.05M K^{+} . However, comparison of Figures 8, 9 and Table 4 shows good correlation between the elemental analysis of the filtered coal residues and the cation adsorption results obtained by analysis of the filtrates using atomic absorption spectrophotometry. It is observed from Table 4 that for the demineralized coals, calcium uptake increased in the order: pH 1 < pH 6 < pH 10, whereas potassium uptake followed the order: pH 1 < pH 6 = pH 10. The similar potassium loadings at pH 6 or pH 10 suggests that maximum potassium uptake is achieved around pH 6 and further increase in pH does not promote additional adsorption. This phenomenon may be due to saturation of the absorption sites by potassium.

4.4 Char Gasification

The carbon burn-off in carbon dioxide as a function of reaction time is shown in Figures 13 - 15 for the demineralized calcium-loaded coals, while those for the demineralized potassium-containing coals is shown in Figures 16 - 18. The results of carbon gasification for the Dem bituminous coal simultaneously loaded with calcium and potassium are provided in Figure 19.

Figure 13. Dependence of burn-off on reaction time for the Dem lignite loaded with calcium.

Figure 14. Dependence of burn-off on reaction time for the Dem subbituminous coal loaded with calcium.

Figure 15. Variation of carbon burn-off with reaction time for the Dem bituminous coal loaded with calcium.

Figure 16. Burn-off versus reaction time plot for Dem lignite loaded with potassium.

Figure 17. Burn-off versus reaction time plot for Dem subbituminous coal loaded with potassium.

Figure 18. Burn-off versus reaction time plot for Dem bituminous coal loaded with potassium.

Figure 19. Burn-off versus reaction time plot for Dem bituminous coal simultaneously loaded with calcium and potassium.

Analysis of Figures 13 - 15 show that the burn-off for the unloaded demineralized lignite, subbituminous and bituminous coals after about 2 hours are 45%, 40% and 20%, respectively. This is consistent with the observation of Heinemann et al.¹⁸ who reported that the ease of gasification increases in the order : Lignite > Subbituminous > Bituminous chars. Another observation made from Figures 13 - 15 is that for the unloaded demineralized coals, an approximate linear relationship exists between carbon burn-off (%) and reaction time. Figures 13 - 15 show that for the calcium-loaded demineralized coals, gasification rates increase according to the following catalyst loading pHs: pH 6 > pH 10 > pH 1.

The metal uptake data in Table 4 show that for all the demineralized coals, maximum calcium loading (% wt.) is achieved at pH 10 followed by pH 6 and it is minimum at pH 1. It will be expected that the gasification rates will also follow a similar order. However, the calcium loading at pH 10 produced char reactivities that are intermediate between those loaded at pH 6 and pH 1. The unexpected reduction in the gasification rates of chars loaded with catalysts at pH 10 may be due to reduced catalyst dispersion or pore plugging by the high calcium content which reduces access of carbon dioxide to the pores of the chars. Serio et al.⁴⁸ have observed that significant change in reactivity occurs when the calcium content of a demineralized Zap Indian Head lignite increases from 0.01 wt % to 1.65 wt %. The catalysts were loaded from 0.05M calcium acetate solution. Further increases in calcium loading level did not cause any marked increase in reactivity, possibly due to pore plugging.

It is observed from Figures 16 -18, that for the potassium loaded demineralized coals, with the exception of the lignite, the gasification rates generally increase according to the following catalyst loading pHs: pH 6 $\approx$ pH 10 $\gg$ pH 1. This trend follows the potassium adsorption capacities reported in Table 4: pH 6 $\approx$ pH 10 $\gg$ pH 1. Hence there is good correlation between coal gasification rate and the quantity of potassium adsorbed by the coal. Anomalous behavior is observed for the demineralized lignite char containing potassium loaded at pH 1. For reaction times less than about 85 minutes, the carbon burn-off is lower than the corresponding values for catalyst addition at pH 6 or pH 10. But after this time, carbon gasification for the coal loaded at pH 1 is greater than that exchanged with potassium at pH 6 or pH 10. In order to check reproducibility, the pH 1 sample was run four times, once from a new sample batch. Almost identical results were obtained in each case. A possible reason for the high gasification rate of the demineralized lignite char (loaded with potassium at pH 1) could be the predominating influence of reactive surface area (RSA) on char conversion. Jiang and Radovic⁵¹ have found that for calcium loaded lignite chars, both the reaction rate and the reactive surface area (RSA) increased monotonically with carbon conversion.

Figures 16 - 18 show that the burn-off patterns of the demineralized potassium loaded chars at pH 6 and pH 10 are similar. For these samples (Figures 16 - 18) the burn-off (%) first increases sharply to about 80% wt. in the first 30 minutes and then remains steady for the rest of the reaction time. At the end of the two hour gasification period and upon cooling to room temperature, the

residues from the gasification reactions appeared white in color. It is postulated that the solids were residual catalytic materials. It is observed from Figure 19 that the demineralized bituminous coal is less reactive than the raw bituminous. Radovic et al.⁵² have observed that demineralized North Dakota lignite was about 30 times less reactive than the raw lignite. This phenomenon has been ascribed to the removal of the inorganic materials, some of which have catalytic activity.¹⁵

Comparing the gasification rates for the calcium and potassium loaded chars (Figures 13-18), it is observed that the potassium loaded chars have higher carbon burn-off rates than the calcium loaded samples. The maximum burn-off for the calcium loaded chars is 70% wt. while it is 80% wt. for chars derived from potassium loadings at pH 6 or pH 10. This confirms previous studies which show that potassium is a more active catalyst than calcium for the gasification of the coal chars.²⁶ This is also consistent with the results obtained by Hippo et al.¹⁵ according to which the reactivities in steam of chars derived from acid leached coals followed the order: $K > Na \approx Ca > Fe > Mg$.

It is observed from Figure 19 that the demineralized bituminous char loaded simultaneously with calcium and potassium at pH 0.9 has a maximum char burn-off of about 98% wt. But the corresponding chars prepared from the pH 4.9 and pH 8.6 samples have lower peak burn-off values.

In order to determine if the char gasification conditions were pore diffusion limited, samples of the lignite, subbituminous and bituminous chars obtained from the calcium-exchanged coals (at pH

10) were subjected to CO₂ gasification using different initial weights. It was observed that initial weight had no effect on the burn-off rates. The carbon burn-off values were almost identical for different initial weights of a sample. Hence it is concluded that pore diffusion limitations were absent under the char gasification conditions examined.

The reactivities of the various demineralized chars were computed from the carbon burn-off versus time plots using the following relationship (equation 17) at 1.5 hours of reaction:⁵³

$$R = 1/w [dw/dt] \quad (17)$$

where R is the reactivity, w is the initial weight of the char, [dw/dt] is the rate of char gasification at 1.5 h. The reactivities for the various demineralized chars are shown in Table 5.

TABLE 5

Reactivities for various chars at 1.5 h

Dem Coals	Metal	pH*	Reactivity (h^{-1})
Lignite	Ca	1	0.28
Lignite	Ca	6	0.44
Lignite	Ca	10	0.33
Subbituminous	Ca	1	0.16
Subbituminous	Ca	6	0.31
Subbituminous	Ca	10	0.25
Bituminous	Ca	1	0.06
Bituminous	Ca	6	0.23
Bituminous	Ca	10	0.25
Lignite	K	1	0.53
Lignite	K	6	0.49
Lignite	K	10	0.52
Subbituminous	K	1	0.18
Subbituminous	K	6	0.71
Subbituminous	K	10	0.60
Bituminous	K	1	0.16
Bituminous	K	6	0.47
Bituminous	K	10	0.29
Bituminous	Ca+K	0.9	0.55
Bituminous	Ca+K	4.9	0.38
Bituminous	Ca+K	8.6	0.40

*Minimum pH variation is ± 0.2 *Maximum pH variation is ± 0.6

The reactivities of the demineralized lignite, subbituminous and bituminous coals with no metal loading and no pH control are 0.22, 0.18 and 0.11 h^{-1} , respectively. In contrast, the reactivities of the lignite, subbituminous and bituminous coals are 0.49, 0.71 and 0.47

h^{-1} , respectively, for potassium addition at pH 6. Hence the reactivities of demineralized coals are dependent on nature of metal catalyst and the pH at which the metal is loaded. The data in Table 5, shows that, in general, reactivity increases with increasing catalyst loading except at pH values above 6. Wigmans et al.⁵⁴ also have found that a high initial catalyst (K_2CO_3) loading produces higher initial and maximum reactivities. The general trend from the data in Table 5 is that the potassium loaded samples have higher reactivities than those containing calcium. The trend is also pH dependent. Therefore, the reactivities are dependent on the metal catalyst and the catalyst loading pH.

4.5 Environmental Scanning Electron Microscopy (ESEM)

Figure 20 shows the ESEM photograph of the calcium loaded demineralized lignite at pH 6 ± 0.6 .

Figure 20. ESEM photograph of Dem lignite loaded with 4.3% wt. of calcium at pH 6.

No definite calcium catalyst particles could be observed from Figure 20. This suggests that the calcium particles are very fine and uniformly dispersed on the coal surface. The lowest detection limit of the ESEM is 50Å. Previous work by Takarada et al.¹⁶ did not reveal potassium catalyst on chars examined by Scanning Electron Microscopy (SEM) since the potassium catalyst particles were highly dispersed on the char surface.

4.6 Energy-Dispersive X-ray Microanalysis (EDXRM)

Figure 21 shows the X-ray microanalysis results for the calcium loaded demineralized lignite at various pHs while Figure 22 gives the analysis for the calcium loaded demineralized bituminous coal at three different points on the same particle.

pH 1

pH 6

pH 10

Figure 21. X-ray microanalysis of Dem lignite loaded with calcium at pH 1, 6 and 10.

Point 1

Point 2

Point 3

Figure 22. X-ray microanalysis of calcium loaded Dem bituminous coal at pH 6. The analysis was done at three different points on the same particle.

It is observed from Figure 21 that the calcium loaded demineralized lignite at pH 1 has the lowest calcium content while the corresponding coal at pH 10 has the highest calcium content. This correlates with the elemental analysis and the cation adsorption results discussed previously. From Figure 22 it is observed that the amounts of calcium on three different points on one particle is almost identical, suggesting a uniform calcium catalyst dispersion on the coal surface.

4.7 X-ray Diffraction Analysis

In order to gain insight into the catalyst dispersion and composition, samples of the lignite and the subbituminous coal loaded with calcium at pH 1, 6 and 10 and examined using X-ray diffraction. The diffraction pattern obtained for the lignite is shown in Figure 23. Similar results were obtained for the subbituminous coal.

Figure 23. X-ray diffraction pattern for the Dem lignite loaded with calcium at pH 1, 6 and 10.

Analysis of Figure 23 shows that peaks corresponding to calcium carbonate (29.4°) and calcium oxide (37.4°) are present for the sample exchanged with calcium at pH 10, but absent for the other pHs. The lack of diffraction patterns is attributed to a high catalyst dispersion at the lower pHs whereas the diffraction peaks are indicative of reduced catalyst dispersion. This confirms the lower char reactivity for the pH 10 sample. Hence at lower pHs the calcium oxide or calcium carbonate is highly dispersed on the coal surface so that their crystallite size is below the detection limit of the instrument. A particle size of 5nm is usually cited as the lower X-ray diffraction (XRD) detection limit for supported metal catalysts.⁵² The above XRD peak assignments agree with earlier work done by Radovic et al.⁵², who also observed diffraction peaks centered around 29.4° and 37.4° for demineralized lignites loaded with calcium. The broad peaks around 21.5° are characteristic of highly disordered carbonaceous materials.⁵¹

4.8 Surface Area Analysis

Figure 24 shows the variation of surface area as a function of pH for raw and demineralized bituminous coals loaded with 0.05M calcium and demineralized bituminous loaded with 0.05M potassium.

Surface Area of Raw Bituminous Coal = $6.1 \text{ m}^2/\text{G}$
 Surface Area of Dem Bituminous Coal = $0.55 \text{ m}^2/\text{G}$

Figure 24. Variation of coal surface area with catalyst loading pH.

It is observed from the figure that there is no appreciable variation of surface area with pH. This trend is typical for the other coals. Similar findings have been observed by Serio et al.,⁴⁸ who found no significant differences between the surface areas for raw and calcium-loaded coal samples. Hegermann and Huttinger⁵⁵ concluded that BET surface area has minor influence on char reactivity. Hence it is possible that surface area is not a limiting factor in the char gasification reactivities observed in this study.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Conclusions

For the first time, the influence of measured coal surface charge on the adsorption of calcium or potassium from solution prior to gasification has been investigated. The char reactivity studies focused on the demineralized derivatives of three ranks of coal: a lignite, subbituminous and bituminous coals and their demineralized derivatives. Surface charge determination were conducted on the raw and the acid-leached coals to ascertain the effects of demineralization on the surface electrical properties of the coals. Zeta potential measurements showed that the surfaces of the raw and demineralized coals acquire a net negative charge over a wide range of pH. The negative charge density increased as the pHs of the coal dispersions were altered from very acidic to strongly basic conditions. Demineralization increased the net negative charge densities compared to the original subbituminous and the bituminous coals while the opposite effect was observed for the lignite.

To minimize the interference of the inherent inorganic materials of the coals with the added calcium or potassium, the gasification studies were restricted to the demineralized (Dem) coals. Calcium or potassium was ion-exchanged onto the Dem samples at about pH 1, pH 6 and pH 10. In strongly acidic environments ($\approx$ pH 1), calcium or potassium uptake was very low (0.1 - 0.4% wt.), suggesting minimal electrostatic attraction between the cations and the slightly negatively charged coal surface. However, metal

adsorption increased dramatically as the pHs of the slurries were raised to pH 6 or 10. On the average, the amount of calcium exchanged onto the coals increased from 0.2% to 3.5% wt. of Ca (a 17.5 fold increase) by changing the pHs of the coal slurries from pH 1 to pH 6, while the calcium content doubled to an average value of 7.0% wt. Ca when the pH was increased from 6 to 10. Potassium uptake followed the order: pH 6 $\approx$ pH 10 $\gg$ pH 1, the average potassium concentration in the coals being 0.2% and 2.5% wt. K at pH 1 and pH 6, respectively. Compared to potassium, the higher calcium loadings at near neutral and in basic solution is attributed to the divalent nature of the calcium ion (Ca^{+2}) which promotes a stronger coulombic attraction to the negatively charged coal surface than the monovalent potassium ion (K^{+}).

The reactivities of the calcium or potassium-containing chars in CO_2 at 1073 K were also strongly dependent on the pHs at which the metals were exchanged onto the coals. Char reactivities in the presence of calcium generally increased in the order pH 6 > pH 10 > pH 1 whereas for potassium the reactivities followed the trend pH 6 $\approx$ pH 10 $\gg$ pH 1, consistent with the potassium contents. The reduction in the catalytic activity of calcium at high metal loadings (5.9, 7.2 and 7.8% wt. Ca) is ascribed to reduced catalyst dispersion. This work also shows that potassium is a more active catalyst for the CO_2 gasification of demineralized samples of a North Dakota lignite, Montana subbituminous and Illinois No. 6 bituminous coals and that char reactivities are dependent on the pH, and hence, on the magnitude of the negative surface charge densities on the coals during catalyst loading from solution. The knowledge gained from

the current work can be used to design more efficient catalysts, predict optimum catalyst loading conditions and to increase catalyst dispersion for enhanced coal char gasification.

Further investigations into the mode of the coal surface functional group-metal interactions are required. Such information may be obtained from X-ray Absorption Fine Structure (XAFS) and Energy Dispersive X-ray Analyses (EDAX). XAFS spectroscopy is a powerful technique that has a unique ability to focus on only one element and provide information about its bonding and short range structure. Qualitative information on the dispersion of calcium and potassium on the coals may be obtained from EDAX. Further work is also required to better understand the effects of coal-catalyst interaction (in solution) on catalyst dispersion, as is the development of improved instrumentation for such studies, since the conventional catalyst dispersion techniques are not readily amenable to coals.

5.2 Publications Resulting from the Study

1. Abotsi, G. M. K., Bota, K. B. and Saha, G., "The Influence of Coal Surface Chemistry on the Adsorption of Coal Conversion Catalysts," American Chemical Society, Division of Fuel Chemistry Preprints, **35(3)**, 606-610, 1990.
2. Abotsi, G. M. K., Bota, K. B. and Saha, G., "Relationships Between Coal Surface Chemistry, Catalyst Adsorption, and Char Reactivity," 20th Biennial Conference on Carbon, American Carbon Society, Extended Abstracts, 460-461, 1991.
3. Abotsi, G. M. K., Bota, K. B. and Saha, G., "Enhancement of Coal Gasification Activity by Coal-Catalyst Interactions," International Conference on Coal Science Proceedings, International Energy Agency, Butterworth-Heinemann, London, 412-415, 1991.

4. Abotsi, G. M. K., Bota, K. B. and Saha, G., "Effects of Coal Surface Charge on the Adsorption and Gasification Activities of Calcium and Potassium," *Fuel Science and Technology International*, in press.
5. Abotsi, G. M. K., Saha, G., and Bota, K. B., "Interfacial Phenomena in Coal Impregnation with Catalysts," *Energy & Fuels*, in press.
6. Bota, K. B. and Abotsi, G. M. K. "Ammonia: A Reactive Medium for Catalyzed Coal Gasification," submitted to *Applied Catalysis*.

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