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THE ROLE OF CATALYST PRECURSOR ANIONS IN COAL GASIFICATION

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CONTENTS

	Page
Summary	i
CHAPTER 1	1
SURVEY OF RELEVANT LITERATURE	1
1.1 Introduction and Statement of the Problem	1
1.2 Catalysis in Coal Liquefaction	1
1.3 Reactions and Mechanisms of Coal Liquefaction	3
1.4 Effects of Catalyst Precursors	4
1.5 Coal Surface Electrochemistry	5
1.6 Coal Surface Charge Measurement	7
1.7 Catalyst Interaction with Coal Surface	7
1.8 Statement of Work	9
CHAPTER 2	10
EXPERIMENTAL SECTION	10
2.1 Coal Demineralization	10
2.2 Zeta Potential Studies	11
2.3 Catalyst Loading	12
2.4 Mechanism of Catalyst Adsorption	13
2.5 Surface Area Analysis	13
2.6 Char Gasification	14
CHAPTER 3	16
RESULTS AND DISCUSSION	16
3.1 Electrokinetic Properties of the Coal in Catalytic Salt Solutions	16
3.2 Catalyst Adsorption	34
3.3 Surface Area of the Coals	40
3.4 FT-IR Studies	42
3.5 Char Gasification	42
3.6 Summary and Conclusions	53
3.7 References	57

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Summary

It is generally known that salts of the same metal exhibit different char reactivities under similar reaction conditions. Whether anions influence catalyst (metal ion) loading from solution is unknown. This study focused on the catalytic effects of the salts of calcium and potassium: (i) calcium acetate, calcium chloride or calcium nitrate and (ii) potassium acetate, potassium carbonate, potassium chloride, potassium nitrate, or potassium sulfate. The effects of these salts on the surface electrical properties and metal loading capacities of a lignite and its demineralized derivative were also studied. Zeta potential results showed that the net negative charge density on the coal particles was reduced by addition of each salt. This effect was more prominent for the calcium compounds than for the potassium-containing precursors. Cation loading by ion-exchange was dependent on both the catalyst precursor (anion) and the metal ion (cation). In general, the calcium adsorption capacity was higher than that for potassium under similar solution conditions. The maximum calcium loading occurred from calcium acetate solution whereas approximately the same but smaller level of calcium was adsorbed from the calcium chloride or the calcium nitrate solution. Potassium uptake followed the order: carbonate > acetate > nitrate ~ chloride ~ potassium sulfate. FT-IR spectra have shown that Ca^{2+} or K^{+} was exchanged for the protons on the coal surface carboxylic acid functionality.

Consistent with zeta the potential data and the catalyst metal adsorption results, the reactivities of the chars generally increased with increase in catalyst loading. However, when the char conversions were normalized to reactivities per gram of catalyst adsorbed, the gasification rates decreased with increase in catalyst loading, suggesting reduction in catalyst dispersion with increase in catalyst content or the effects of mass transfer limitations during char gasification. Char reactivity by potassium carbonate was lower compared to the other catalytic salts. This could be due to the higher potassium content of the coal and the resultant more sintering of the catalyst at the gasification temperatures. The availability of techniques for catalyst dispersion measurement on coal should increase our understanding of the relationship between coal surface chemistry, catalyst loading and dispersion and char gasification.

For the first time, the effects of various salts on the electrokinetic properties of coal and its influence on catalyst precursor (metal ion) adsorption prior to coal gasification has been investigated. It has been shown that coal surface chemistry and metal ion adsorption is dependent on the salt applied. Thus, catalyst (metal ion) loading from solution should involve determination of the solution parameters such as pH which will ensure optimum cation uptake and catalyst dispersion on coal.

CHAPTER 1

SURVEY OF RELEVANT LITERATURE

1.1 Introduction and Statement of the Problem

The utilization of coal is currently limited by several factors, including the environmental impacts of coal use and the lack of cost-effective technologies to convert coal into useful gaseous and liquid products. Several catalysts have been evaluated for coal gasification and liquefaction. The activities of the catalysts are dependent on many factors such as the method of catalyst addition to the coal and the catalyst precursor type. Since catalyst addition to coal is frequently conducted in aqueous solution, the surface chemistry of colloidal coal particles will be expected to exert an influence on catalyst uptake. However, the effects of the various coal gasification catalyst precursors on the interfacial properties of coal during catalyst loading from solution has received little attention.

The aim of this study is to ascertain the influence of the metal salts (i): calcium acetate ($\text{Ca}(\text{OOCCH}_3)_2$), calcium chloride (CaCl_2) or calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and (ii): potassium acetate (KOOCCH_3), potassium chloride (KCl), potassium nitrate (KNO_3), potassium carbonate (K_2CO_3) and potassium sulfate (K_2SO_4) on the electrokinetic and adsorptive properties of coal and determine the relationship, if any, between coal surface electrokinetic properties, and catalyst loading and eventually its effects on the reactivities of coal chars.

1.2 Catalysis in Coal Gasification

A wide range of metal salts, principally the carbonates, halides, nitrates, oxides and sulfates have been investigated for their catalytic effects on coal gasification¹⁻⁴. In general,

the alkali and alkaline earth metal halides are typically the most effective. Alkali and alkaline earth metal acetates, nitrates and sulfates are less active than the metal carbonates and hydroxides.⁵⁻¹⁰ Among the transition metals, iron has been shown to be an attractive catalyst for coal gasification¹¹⁻¹⁴. Mixtures of FeSO_4 and K_2SO_4 have also been reported to be effective for carbon gasification^{12,15}. Hippo et al¹¹ have shown that, compared to calcium, magnesium and sodium, iron is a more active catalyst for short residence time steam gasification (at 923K) of chars produced from a lignite. The decline in catalyst activity with increase in reaction time was attributed to the transformation of iron into Fe_3O_4 and Fe_2O_3 , as determined from x-ray diffraction analysis. Other workers¹³ have attributed the reduction in the activity of iron towards carbon gasification in water vapor or hydrogen to reduced catalyst dispersion as a result of the sintering of the iron particles. Like other char gasification catalysts, the effects of these salts on the surface chemistry of coal in aqueous solution has not been studied, although the catalysts are normally loaded from solution.

Char gasification is usually attributed to the metal component of a catalyst precursor^{1-4,16-19}. The activities of the catalysts can be influenced by the inorganic materials in the coal, which can react with the catalyst as exemplified by the reaction of K_2CO_3 with clay minerals (e.g., illite and kaolinite) to form kaliophilite:

It is also well known that different catalytic salts containing the same metal produce significantly different char reactivities under similar reaction conditions. A comparative study on the acetates, chlorides and hydroxides of calcium, magnesium, potassium and sodium has shown that the catalysts exhibit distinct char gasification activities under similar reaction conditions¹⁹. The catalysts were loaded from aqueous solution. It has been shown, for instance, that at 1223K, the order

of reactivity for the sodium compounds was $\text{NaOH} > \text{NaAc} > \text{NaCl}$. These findings were rationalized in terms of the influence of the various anions on the diffusivities of the cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+} produced by dissociation of the metal precursors at gasification temperatures) through the pores of the chars.

1.3 Reactions and Mechanisms of Coal Gasification

The carbon in coals and chars can be converted to gaseous products by reaction with oxygen, steam, carbon dioxide or hydrogen. Equations (2) - (5) show the reactions of the commonly used gases with carbon. The gasification of coal chars in ammonia has been reported recently, the major products being cyanogen and hydrogen²⁰. The reaction is depicted in equation (6):

A number of reaction mechanisms have been proposed for char gasification in the various gaseous reactants. Wigmans et al.²¹ have proposed the following steam gasification mechanism of carbon in the presence of metal catalyst, M, as represented by equations (7)-(10):

From the above mechanism, it was proposed that coal-oxygen-metal (C-O-M) surface complexes are essential prerequisites for char reactivity^{9,10,21-24}. It has been reported that high initial gasification activities were obtained for oxygen-containing salts of potassium or sodium (K_2CO_3 , KNO_3 , KOH , K_2SO_4 and Na_2CO_3). However, introduction of KCl or $NaCl$ gave low initial char conversion rates but the rate increased gradually as gasification proceeded. The gradual increase in gasification rate was attributed to the reaction of these salts with steam to form carbon-oxygen-metal bonds²⁵. Thus, steam is required for the activation of KCl and $NaCl$ catalysts. Hence, it is possible that metal halides do not possess any inherent catalytic activity for gasification.¹ Evidence for this conclusion has been given by Mims et al.²⁶ who converted the K_2CO_3 impregnated on amorphous carbon to KCl by reaction with HCl at 573 K. They found that the catalytic activity of K_2CO_3 was destroyed by HCl . It has also been suggested that the metal in the catalytic salt reacts with the carbon in the char to form active intermediates for gasification. The metal is generally considered the catalyst and the anion favorably modifies the structure of the active species. However, the composition and structure of the active intermediates are unknown²⁶.

1.4 Effects of Catalyst Precursors

The effectiveness of a catalyst has been shown to be dependent upon the cation of the catalyst precursor. 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 investigators²⁷⁻³³ have examined iron and nickel compounds as gasification catalysts. It has been concluded that these metal catalysts generally exhibit lower gasification rates compared to alkali and alkaline earth carbonates.¹⁵ Walker et al.³⁴ have reported

that calcium is the most important catalyst for gasification of chars derived from raw coals when using air, carbon dioxide or 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.³⁵ 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.³⁶ have compared the effectiveness of potassium carbonate and hexamine nickel carbonate as catalysts in gasification. It was concluded that potassium was a more active catalyst than nickel and the activity of the former was independent of coal rank whereas the effectiveness of nickel depends on the coal type. Sams et al.³⁷ have shown that the catalytic effect of potassium on the rate of char gasification in CO₂ increases sharply at low values of K/C atomic ratio (0.019-0.035). As the 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 in reaction rate is also possibly due to the plugging of the micropores by the catalysts. Heinemann et al.³⁸ 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.

1.5 Coal Surface Electrochemistry

Low rank coals contain surface groups such as carboxylic acids and phenolic functional groups.³⁹⁻⁴¹ In aqueous and basic media, these acidic surface groups dissociate and the coal particles acquire net negative charges as shown in equations (11) and (14). 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).^{40,41} 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 ($\text{pH} < 7$). At the isoelectric point, the net surface charge will be zero.⁴² 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 is a function of coal slurry pH and its isoelectric point.

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.⁴³⁻⁵⁰ Hence, control and modification of the pH of catalyst impregnating solutions is crucial in order to maximize metal ion adsorption onto coal and possibly enhance initial catalyst dispersion.

1.6 Coal Surface Charge Measurement

The determination of coal surface charge of particles in solution may be accomplished by measuring the zeta potentials of the coal particles. To determine the zeta potential, which is directly related to the surface charge density, the coal-water slurry is placed in a sample chamber consisting of two electrode compartments and a connecting chamber. When a voltage is applied between the two electrodes, a uniform electric field in the connecting chamber is induced and the suspended coal particles migrate 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 (15):

$$V = DX\xi/4\pi\mu \quad (15)$$

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.⁵¹ 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.

1.7 Catalyst Interaction with Coal Surface

The reaction of gases with carbon, as studied using a microscope, have shown that the regions of enhanced carbon gasification are the interface between the carbon and the added catalyst particles.⁵²⁻⁵⁴ 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.³⁵ In this technique the protons on coal particles are displaced by the metal ions. Such an exchange occurs in nature when ground water saturated with calcium, potassium, sodium, magnesium ions or other metal ions percolates 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.^{29,55} 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.⁵⁶ 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.¹⁰ have attributed these peaks to K-O-C bonds, and hence it was concluded that metal (M) is bonded to oxygen in the form of M-O-C bonds on the carbon surface. The oxygen in M-O-C could arise from the catalyst precursors or from the coal surface acidic groups.

From electron spin resonance (ESR) measurements, Sancier⁵³ and Wood et al.²⁵ 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 600K. 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. It was suggested that this was a strong indication of an interaction between the catalyst and the carbon.

In synopsis, the results of several studies have shown that, in general, effective coal char or carbon gasification catalysts are ionic salts with oxyanions. These studies also suggest that the cations of the salts react with the carbonaceous material to form chemically and thermodynamically distinct active species that mediate the gasification process.

1.8 Statement of Work

The main goal of this research is to enhance our understanding of the roles of cations and anions of catalytic salts during metal ion (cation) loading onto coal from solution. Specifically, the effects of various catalytic salts on the electrokinetic properties of coal and its adsorption of cation will be determined. The study will be conducted on the calcium or potassium salts: calcium acetate, calcium chloride or calcium nitrate and potassium acetate, potassium carbonate, potassium chloride, potassium nitrate, or potassium sulfate. The effects of the metal ions (Ca^{2+} or K^{+}) or anions ($\text{CH}_3\text{COO}^{-}$, CO_3^{2-} , Cl^{-} , NO_3^{-} , and SO_4^{2-}) on the zeta potentials of a lignite and its demineralized derivative will be evaluated to determine the influence of coal surface chemistry on cation uptake. The mechanism of cation loading onto the coals will be determined using FT-IR. The char gasification activities of the catalysts will be evaluated in carbon dioxide at 700°C . The experimental techniques applied in the investigations are discussed in Chapter 2.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 Coal Demineralization

Samples of a lignite obtained from North Dakota Hagel seam were used for the study. The proximate and ultimate analyses of the as-received coal are provided in Table 1.

Table 1. Properties of the lignite used.

<u>Proximate analysis, % wt.</u>		<u>Ultimate analysis, %wt (daf)</u>	
Moisture	34.5	C	71.3
Volatile matter	28.2	H	4.5
Fixed carbon	31.8	N	1.1
Ash	5.6	S	0.8
		O (by diff.)	22.3

The inorganic matter of the original coal (supplied in sealed argon atmosphere by The Pennsylvania State University Coal Sample Bank and code-named PSOC 1482) was minimized by leaching in hydrochloric and hydrofluoric acid solutions for several weeks. Portions of the raw lignite were demineralized with equal volumes of concentrated HCl and HF. Sufficient amounts of the acids were added so that the raw coal was completely submerged in the acid solution. 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. After leaching, the coals were filtered through a

Buchner Funnel and washed repeatedly with distilled water until the pH of the filtrate was close to 6 and the filtrate was virtually colorless. The demineralized coals were then dried in a vacuum oven at 343 K for about two hours. Acid leaching: converts the surface carboxylates to carboxylic acid,³⁵ removes mineral oxides such as silicates and aluminosilicates,³⁵ and increases the carboxyl content of coals by leaching multivalent cations from the coal.⁵⁴

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. Hence, the demineralized coal provided a reference background for comparison.

2.2 Zeta Potential Studies

Zeta potential measurements were conducted as a function of coal slurry pH on -200 mesh size sieve (75 μm) particles of the parent or the acid-leached coal. Each slurry was prepared using 300 mg of coal per liter of aqueous solution; the ionic strength was controlled with 10^{-3} mol/L NaNO_3 . High dispersion of the coal particles was achieved by vibrating in a "Branson 2200" ultrasonic bath for about 10 minutes. After allowing 5 min for the heavier particles to settle, the top portion of the dispersion was decanted and divided into 50.0 mL units and their pHs were controlled with nitric acid or ammonium hydroxide solution. The strongly acidic or basic pHs were adjusted with 15.8 mol/L HNO_3 or 12.1 mol/L NH_4OH solutions, respectively. The intermediate pHs were controlled using 0.1 mol/L solution of the acid or base. All pH measurements were done with the aid of a "Fisher Scientific Accumet 910 pH Meter" which had been standardized with pH 4, 7 or 10 buffer solutions. The coal suspensions were equilibrated by mechanical agitation for 4 hours after which the zeta potentials were measured using a Pen Kem model 501 "Laser Zee Meter."

The zeta potential measurement involves suspending the fine coal particles in an aqueous solution contained in a chamber to which an anode and a cathode are connected. To avoid interference with particle mobility, air bubbles were eliminated from the sample cell by tilting it and slowly injecting the slurry with a syringe. The chamber was then transferred to a microscope stage interfaced with the laser meter and the microscope was focused on the particles. Application of an electric voltage created a potential between the electrodes, causing the particles to migrate to the anode or the cathode -- negative particles towards the anode and positive ones to the cathode. A cube prism inside the microscope caused the particle's image to translate at a rate proportional to the prism's speed of rotation. The colloidal particles appeared stationary when the image velocity due to prism rotation was equal and opposite to the mean electrophoretic mobility. The zeta potential was computed from the mean particle mobility and displayed on a digital meter. A similar procedure was used to determine the electrokinetic properties of aqueous suspensions of the demineralized coal containing 10^{-3} , 10^{-2} or 10^{-1} mol/L of calcium acetate ($\text{Ca}(\text{OOCCH}_3)_2$), calcium chloride (CaCl_2), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), potassium acetate (KOOCCCH_3), potassium carbonate (K_2CO_3), potassium chloride (KCl), potassium nitrate (KNO_3) or potassium sulfate (K_2SO_4).

2.3 Catalyst Loading

Since the quantity of coal sample used for the zeta potential studies was insufficient for chemical analysis, 4.0 g of the demineralized coal were dispersed in 100.0 mL of solution containing 10^{-3} or 10^{-1} mol/L of each salt to determine the extent of catalyst adsorption. The samples were filtered after 24-hour agitation on a mechanical shaker to effect cation adsorption by the coal. The calcium or potassium content of the filtered coal particles (vacuum dried at 323K) was measured (by Galbraith Laboratories, Inc., Knoxville, TN) using inductively coupled argon plasma emission spectroscopy or atomic

absorption spectrophotometry, respectively. Samples for the chemical analyses were prepared by fusion in lithium metaborate at 1273K followed by dissolution of the melt in a solution containing 3% nitric acid, 3% tartaric acid and hydrogen peroxide.

2.4 Mechanism of Catalyst Adsorption

The mechanism of metal uptake was studied using Fourier transform infrared spectroscopy (FT-IR). Coal-KBr pellets were prepared using one milligram of coal dispersed in 300 mg of spectral grade KBr and dried at 323K in partial vacuum. FT-IR is a powerful tool for studying the atomic vibrational modes of the structure of molecules. When radiated with infrared beams, molecules absorb some of the electromagnetic radiation which induces changes in the vibrational energy levels of the molecules and results in the production of spectra. The spectral bands are specific for each functional group, and this allows observation of the molecular structures or structural changes associated with chemical reactions involving functional groups⁵⁷.

2.5 Surface Area Analysis

The surface areas of the unloaded and the metal-containing samples were measured by nitrogen adsorption at 77K using a Micromeritics Gemini 2360 surface areameter. The measurements were conducted on about 0.5 g of coal which had been degassed in helium at 383K. The data were analyzed using the Brunauer, Emmet and Teller (BET)⁵⁸ equation.

Surface area analysis was chosen as one of the analytical techniques to study the catalyst-containing coals in order to determine any correlation between surface area, pH of catalyst solution and coal char gasification activity. The surface area analysis is based on gas adsorption to monolayer capacity of the coal surface.

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 absorbing 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:

$$P/V(P_0-P) = 1/V_m C + (C-1)P/V_m C P_0 \quad (16)$$

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 $0.05 < P/P_0 < 0.35$. 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.⁵⁹

Multiple point BET surface area analyses were conducted on the catalyst-loaded and unloaded coals using a "Micromeritics Flowsorb 2300" surface area analyzer. All samples were degassed overnight before performing the surface area measurements. Adsorption was performed at a temperature of -195°C (temperature of liquid nitrogen). Nitrogen gas was used as adsorbate, and a N_2 cross-sectional surface area of 0.162 nm^2 was used in calculating the surface areas of the coals⁶⁰.

2.6 Char Gasification

The effects of the various catalyst precursors on char reactivity were studied in carbon dioxide. A Dupont 951 thermogravimetric analyser (TGA), interfaced with a microcomputer, was used to measure the weight changes during the gasification reactions. About 20 mg of the demineralized, unloaded coal sample were placed in a platinum pan and flushed with nitrogen at room temperature for 15 min. The samples were then pyrolyzed by

heating at 20°C/min. from room temperature to 700°C in a continuous flow of nitrogen and holding at this temperature for 30 min. Char reactivity was initiated by replacing the N₂ supply with a 100 cm³/min. of CO₂. Carbon gasification was allowed to proceed for about 1h. The reaction was repeated on the coal samples that have been ion-exchanged with the catalytic salts.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Electrokinetic Properties of the Coal in Catalytic Salt Solutions

The dependence of the zeta potentials on pH are shown in Figure 1 for the raw and the demineralized coals. The isoelectric point (iep) for the raw coal occurs at $\sim$ pH 1.8 while that for the acid-leached coal is estimated at pH 0.5. For both coals, the zeta potentials become more negative as the pH of the slurry is raised from acidic to basic. This phenomenon has been attributed to the dissociation of surface carboxylic and phenolic hydroxyl groups³⁹⁻⁴². It is observed that the demineralized coal is more negatively charged than the raw coal, as indicated by its higher negative zeta potentials at all the pHs investigated. It has been determined that acid-leaching of coal removes metals from humate salts which are then converted to humic acids due to the very low pHs involved^{39,40}. Thus, the elimination of multivalent cations (e.g., Ca^{2+}) from coal increases the concentration of dissociable hydroxyl group compared to that on the unleached coal with the resultant higher negative surface charge density on the demineralized coal.

The zeta potential results for the raw coal in the presence of aqueous solutions of potassium acetate, potassium carbonate, potassium chloride, potassium nitrate and potassium sulfate are shown in Figures 2-6, respectively. The zeta potential trend for the particles in the presence of these salts are similar to those of the raw coal, in that the surface charge density on the colloidal particles become progressively more negative as the pH of the coal slurry is raised from acidic to basic. Figure 2 shows that the zeta potentials of the coal samples are essentially the same between about pH 2-8 for all the potassium acetate concentrations (10^{-1} , 10^{-2} and 10^{-3} mol/L KOOCCCH_3) investigated. The sharp upturn in

Figure 1. Zeta potentials for the lignite and its demineralized derivative as a function of coal slurry pH.

Figure 2. Zeta potential variation for the raw lignite as a function of equilibrium pH and potassium acetate concentration. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KOOCCCH_3 , respectively.

Figure 3. Dependence of zeta potential on equilibrium pH and potassium carbonate concentration for the raw lignite. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L K_2CO_3 , respectively.

Figure 4. Variation of zeta potential as a function of equilibrium pH and potassium chloride concentration for the as-received lignite. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KCl, respectively.

Figure 5. Variation of zeta potential as a function of equilibrium pH and potassium nitrate concentration for the raw lignite. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KNO_3 , respectively.

Figure 6. Variation of zeta potential as a function of equilibrium pH and potassium sulfate concentration for the raw lignite. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L K_2SO_4 , respectively.

the zeta potential at 10^{-2} mol/L KOOCCH_3 around pH 9 is similar to that observed for 10^{-3} mol/L K_2CO_3 (Figure 3) at about the same pH. A similar upturn in zeta potentials have been reported in the literature and it will be discussed later in this report.

Figure 3 shows that, except for the change in the direction of the zeta potential at ~pH 9 in the 10^{-3} mol/L K_2CO_3 solution, the surface charge densities are practically the same for the coal particles in 10^{-3} or 10^{-2} mol/L K_2CO_3 solution. This implies that at these salt concentrations, the effects of the catalyst precursors on the coal surface charge are virtually the same. However, significant reduction in the negative surface charge occurs at 10^{-1} mol/L K_2CO_3 . Since the surface of the as-received coal is negatively charged (see Figure 1), the carbonate anions will be repelled from the coal surface by electrostatic forces. However, the potassium ions (K^+) will be attracted to the negatively charged coal surface, resulting in partial neutralization of the negative charge density. This phenomenon is observed in Figures 4, 5 and 6, although more distinctly in the latter two Figures involving potassium nitrate and potassium sulfate, respectively. In each of these samples (Figures 4-6), the negative charge density on the coal surface progressively decreased as the concentration of the potassium ion is increased by increasing the concentration of the catalytic salt from 10^{-3} to 10^{-1} mol/L. Considering the differences in the extent to which the various catalytic salts influenced the coal surface charge density, it is inferred that the various anions (CH_3COO^- , CO_3^{2-} , Cl^- , NO_3^- , and SO_4^{2-}) influenced the interaction of the potassium ion with the coal surface to different degrees. This in turn, resulted in different levels of potassium adsorption as will be discussed later in this report.

In order to more clearly observe the effects of the various catalytic salts on the electrokinetic properties of the coal, the inherent inorganic matter in the coal was minimized by leaching in acid solutions as described in the experimental section of this report. Hence, the subsequent investigations and discussions are focused on the demineralized coal and the catalyst precursors.

Typical variations of the zeta potentials with catalyst precursor will be compared using calcium nitrate and potassium nitrate, or calcium chloride and potassium chloride. Figures 7 and 8 show that addition of calcium or potassium nitrate decreases the negative zeta potential relative to that of the demineralized coal without salt addition. It is also observed that the coal surface becomes less negatively charged as the concentration of the catalytic salt is increased from 10^{-3} to 10^{-1} mol/L. However, the reduction in the negative zeta potential is more prominent for $\text{Ca}(\text{NO}_3)_2$ than for KNO_3 . For instance, at $\sim$ pH 8-10 and 10^{-3} mol/L calcium or potassium nitrate concentration, the zeta potential in the presence of calcium nitrate is about -40 mV while it is -105 mV when potassium nitrate was used. At the higher salt concentration of 10^{-1} mol/L, the zeta potential values have been reduced significantly to approximately zero and -40 mV for the $\text{Ca}(\text{NO}_3)_2$ and KNO_3 , respectively. Essentially similar trends were observed for calcium chloride and potassium chloride (Figures 9 and 10). These results are in agreement with those reported by Fan et al⁶¹ for a medium volatile bituminous coal for which the zeta potential became progressively less negative with addition of increasing amounts (10^{-4} , 10^{-3} , 10^{-2} mol/L) of sodium chloride.

Yoon and Sabey⁶² have shown from studies on coal flotation in inorganic salt solutions that the effect of an electrolyte on the zeta potential of coal is dependent upon the type of salt used. It has been shown that monovalent sodium chloride compressed the double layer around the coal particles, making them less negatively charged than the coal suspension to which sodium chloride was not added. The iep was pH 4.3 in sodium chloride solution but it decreased to pH 3.4 in the absence of the sodium salt. Lithium sulfate or sodium sulfate both shifted the iep from $\sim$ pH 4.3 to pH 1. The acidic iep shifts were ascribed to specific adsorption of the chloride or sulfate anion onto the coal. It has also shown⁶² that a higher compression of the double layer occurred when divalent magnesium chloride or magnesium sulfate was used, resulting in zero mobility of the coal particles over the entire pH range ($\sim$ pH 2-10) investigated. Lanthanum chloride (LaCl_3) reversed the mobility from negative to positive due to adsorption of trivalent lanthanum ion.

Figure 7. Dependence of zeta potential on equilibrium pH and calcium nitrate concentration for demineralized lignite (A). Plots (B), (C) and (D) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L $\text{Ca}(\text{NO}_3)_2$, respectively.

Figure 8. Dependence of zeta potential on equilibrium pH and potassium nitrate concentration for demineralized lignite (A). Plots (B), (C) and (D) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KNO_3 , respectively.

Except for the raw coal, it was not possible to measure the iep's in this study since the iep's occurred in highly acidic ($< \text{pH } 1$) solutions. At very low pH values the ionic strength of the slurry becomes very high and tends to make the coal suspension heat up quickly, resulting in erratic motion of the particles which hinders accurate zeta potential measurements. However, extrapolation has been used to estimate the iep's for coals under such conditions⁶². Application of this method to Figures 7-10 shows that, in general, the iep's for the coal particles in the salt solutions are shifted to lower acidic pHs compared to that for the coal without salt addition. This suggests specific adsorption of the nitrate or chloride anions. This deduction is applicable to the acetate, carbonate and sulfate anions studied in this work because of the similarities between the zeta potential plots in the presence of these anions and those in Figures 7-10.

Since the demineralized coal particles are negatively charged, the reduction in the net negative surface charge density in the presence of the catalytic salt solutions must arise from adsorption of calcium or potassium ions. Compared to the monovalent K^+ ion, the greater effect of the divalent calcium ion on the zeta potentials is due to higher Ca^{2+} adsorption by the coal. For the divalent Ca^{2+} ion, two negatively charged sites on the coal will be required for its adsorption, whereas only one negative site will be occupied by a K^+ ion. Thus the measured zeta potentials of the coal particles are controlled by both the concentration and the valence of the metal ions.

To eliminate the effects of the valencies of the metal ions, the effects of the anions on the zeta potentials can be compared using the salts containing the same metal. For example, at pH 9 and 10^{-2} mol/L salt concentration, the zeta potentials for calcium nitrate and calcium chloride are -20 and -15 mV, respectively, while they are approximately -85 and -80 mV for potassium nitrate and potassium chloride under the same solution conditions. In general, within the same group (i.e., the calcium or the potassium compounds) there is little difference in the zeta potentials at similar pHs and salt concentrations. It has been reported⁶³ that the positive charge on carbon blacks is reduced

Figure 9. Variation of zeta potential as a function of equilibrium pH and calcium chloride concentration for demineralized lignite (A). Plots (B), and (C) are for 10^{-3} and 10^{-2} mol/L CaCl_2 , respectively.

Figure 10. Variation of zeta potential as a function of equilibrium pH and potassium chloride concentration for demineralized lignite (A). Plots (B), (C) and (D) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KCl, respectively.

by the addition of an electrolyte and that the effectiveness of the surface charge reduction followed the order: $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. Since the coal particles in the current study are negatively charged, this trend was not observed although specific adsorption of the anions could have occurred⁶².

Unlike the rest of the catalytic salts, the general zeta potential trends for the demineralized coal are reversed in potassium sulfate solutions, as shown in Figure 11. The coal particles are apparently more negatively charged, for the most part, in the 10^{-1} mol/L salt concentration than at 10^{-3} mol/L, although the possibility of this being due to experimental artifacts can not be ruled out. As can be seen from Figure 12, similar zeta potentials were obtained for the demineralized coal particles dispersed in 10^{-2} and 10^{-1} mol/L. K_2CO_3 solution. Possible reasons for the upturn in the surface charge densities around pH 7 has been discussed earlier. Figure 13 shows that the zeta potentials for the demineralized coal particles in potassium acetate solutions follow the trends discussed above; the coal surface becomes less negatively charged as the salt concentration is increased from 10^{-3} to 10^{-1} mol/L, the effect being more prominent at the latter solution.

In a recent study involving Upper Freeport medium volatile bituminous coal, Fan et al⁶¹ have shown that the zeta potential of the coal particles in 10^{-3} mol/L potassium or sodium chloride solution decreased progressively as the pH of the coal suspension was raised from about pH 2-10. However, when the same concentration of calcium or magnesium chloride was applied, the zeta potential decreased monotonically to ~pH 9-10 and then increased thereafter. It has been shown^{61,64} that calcium and magnesium hydroxy complexes ($\text{Ca}(\text{OH})^+$, $\text{Mg}(\text{OH})^+$) are formed at about pH 9-11 and the upturn in the zeta potential is due to an enhanced electrostatic attraction between the positively charged metal hydroxy complex and the negatively charged coal surface. It is observed from Figures 7, 9, 10 and 12 that an upturn in the zeta potential occurred around pH 6-8, particularly at 10^{-1} mol/L salt concentration, resulting in maximum zeta potentials at ~pH 10. Thus, the

Figure 11. Dependence of zeta potential on equilibrium pH and potassium sulfate concentration for the demineralized coal. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L K_2SO_4 , respectively.

Figure 12. Dependence of zeta potential on equilibrium pH and potassium carbonate concentration for the demineralized coal. Plots (A) and (B) are for 10^{-2} and 10^{-1} mol/L K_2CO_3 , respectively.

Figure 13. Zeta potential variation for the demineralized coal as a function of equilibrium pH and potassium acetate concentration. Plots (A), (B) and (C) are for 10^{-3} , 10^{-2} and 10^{-1} mol/L KOOCCCH_3 , respectively.

observed upturn in the zeta potential for calcium nitrate or calcium chloride is possibly due to the formation and adsorption of $\text{Ca}(\text{OH})^+$.

The electrical potential on the coal surface decreases rapidly with distance away from the coal surface. The effective thickness, $1/K$, is the distance from the charged surface into the solution within which most of the ionic interactions with the surface occur and is given by⁶⁵:

$$1/K = [(DkT)/(4\pi e^2 \sum C_i Z_i^2)]^{1/2} \quad (17)$$

where D is the dielectric constant of the medium, k is the Boltzmann constant, T is the absolute temperature, e is the charge on the electron and C_i is the molar concentration of an ion with valence Z_i . Thus increasing the concentration of a catalyst precursor and/or the valence of the cation results in compression of the double layer (i.e., a decrease in $1/K$), increases the concentration and interaction of the metal ions with the coal surface and enhances a higher level of metal adsorption.

3.2 Catalyst Adsorption

The calcium uptake by the coal from the 10^{-3} or 10^{-1} mol/L solution of the calcium salts is shown in Figures 14 and 15, respectively. The corresponding data for the potassium salts are presented in Figures 16 and 17. It can be seen from Figures 14 and 15 that, in general, calcium adsorption increased progressively with increase in pH. This correlates the zeta potential results and confirms electrostatic attraction between the negatively charged coal particles and the calcium ions. Figures 14 and 15 shows that at 10^{-3} mol/L, calcium adsorption is higher from the calcium chloride solution than from the calcium acetate or nitrate solution. Essentially similar levels of calcium uptake occurred in the latter solutions. At 10^{-1} mol/L salt concentration, the highest calcium loading occurred when calcium acetate was used, whereas calcium loading from the chloride or the nitrate

Figure 14. Dependence of calcium uptake on catalyst precursor. Initial catalyst salt concentration = 10^{-3} mol/L.

Figure 15. Dependence of calcium uptake on catalyst precursor. Initial catalyst salt concentration = 10^{-1} mol/L.

solution was substantially less, particularly in strongly alkaline media. Based on equation (1), the higher calcium adsorption from the more concentrated solution (10^{-1} mol/L) is due to a greater compression of the double layer around the coal particles than that in the 10^{-3} mol/L solution. Similarly, the higher calcium adsorption compared to potassium can be explained by the same equation and the differences in the valencies of the Ca^{2+} and K^{+} ions.

Figure 16 shows that potassium uptake from all the 10^{-3} mol/L potassium salt solutions occurred within a narrow range ($\sim 0.5 - 0.8\%$ wt.). However, at 10^{-1} mol/L (Figure 17) the potassium uptake shows two distinct features: (1) a strong dependence on coal slurry pH, and (2) a dependence on the potassium salt used. For all the catalytic salts, potassium adsorption was minimum around pH 2, it was maximum at $\sim$ pH 10 and it was intermediate around pH 5 and 6. From Figure 17, it appears that at a given pH, potassium uptake can be classified into three groups according to the potassium precursor used: KCl, KNO_3 and K_2SO_4 fall into one group, while KOOCCCH_3 and K_2CO_3 belong to separate groups. It is evident from Figure 17 that the highest potassium loading was obtained at all pHs when adsorption was effected using potassium carbonate solution. The second highest metal uptake occurred when potassium acetate was used and approximately the same level of potassium was adsorbed from potassium chloride, potassium nitrate and potassium sulfate solutions.

As discussed previously, the zeta potentials were essentially similar within the same group of calcium or the potassium precursors. Thus similar levels of metal loading can be expected from the calcium or the potassium salt solutions. As stated earlier, the slurries for the metals adsorption were much more concentrated (4.0 g coal/100 mL) than those used for the zeta potential measurements (0.3 g coal/L). Hence the surface electrochemistry of the coal may be different for the two slurries. It has been shown^{63,66,67} that the electrophoretic mobilities for dilute suspensions of Pittsburgh seam No. 8 coal differ significantly from those measured for the same coal containing 50% wt. coal slurries. This

Figure 16. Variation of potassium uptake with catalyst precursor type. Initial catalyst salt concentration = 10^{-3} mol/L.

Figure 17. Variation of potassium uptake with catalyst precursor type. Initial catalyst salt concentration = 10^{-1} mol/L.

behavior may arise from the shorter average interparticle distances in concentrated slurries compared to those in dilute dispersions. In addition, the dissolution of coal inorganic matter from the concentrated slurry will increase the ionic strength of the solution and compress the electrical double layer. The leached ions can also be hydrolyzed in solution and then readsorb onto the coal surface and change the surface potential⁶³. The observed disparities in metal uptake may be due to differences in the zeta potentials for the dilute suspensions and the more concentrated slurries used for the metals adsorption.

3.3 Surface Areas of the Coals

The surface area of the as-received coal was about $0.5 \text{ m}^2/\text{g}$. This value was reduced by about 50% after demineralization. The surface area data for the demineralized coal after treatment with selected catalyst salt solutions are shown in Table 2. As can be seen from this data, treatment of the coal with catalytic salt solutions results in significant reduction of surface area. This is attributed to the adsorption of metal ions and the plugging of the coal's pore structure by the adsorbed metal species. The surface areas appear to be independent of the catalyst adsorption pH. Since the surface area of the demineralized coal was very low ($0.5 \text{ m}^2/\text{g}$) the effect of this property on metal adsorption should be negligible.

Table 2. Surface areas of the demineralized coal after adsorption of selected catalytic salts.

<u>Catalytic Salt</u>	<u>BET S.A., m²/g</u>	<u>Adsorption pH</u>
KOOCCH ₃	0.04	1.8
KOOCCH ₃	0.20	5.6
KOOCCH ₃	0.09	9.8
K ₂ CO ₃	0.17	1.7
K ₂ CO ₃	0.02	6.7
K ₂ CO ₃	0.02	10.0
KCl	0.10	2.2
KCl	0.01	5.3
KCl	0.02	9.8
CaCl ₂	0.48	2.0
CaCl ₂	0.20	5.1
CaCl ₂	0.03	9.9

3.4 FT-IR Studies

Figure 18A shows the FT-IR spectrum for the unloaded demineralized coal and its calcium-exchanged samples (Figure 18B-D), with calcium nitrate as the source of calcium. Similar spectra were recorded for the coal after ion-exchange with the other catalyst precursors. The distinct peak around 1725 cm^{-1} for the unloaded coal has been assigned to carboxylic acid group⁶⁸⁻⁷⁰. However, the intensity of this peak progressively diminishes as the quantity of calcium exchanged onto the coal increased from 1.3 to 3.2% wt. Previous work⁶⁸ has shown that the carboxylic acid band around 1725 cm^{-1} on a demineralized brown coal essentially disappeared after barium ion (Ba^{2+}) had been adsorbed onto the coal. It has also been reported that the oxidation of a lignite-derived humic acid increased the intensity of the carboxyl peak at 1725 cm^{-1} due to an increase in the concentration of this surface functionality. The intensity of this peak is decreased considerably upon complexation of the humic acid with iron⁶⁹. Thus, the reduction in the intensity of the carboxylic acid peak with increase in calcium or potassium loading is due to the exchange of Ca^{2+} or K^{+} for the proton on the carboxylic acid group.

3.5 Char Gasification

As stated previously, the chars for the gasification reactions were pyrolyzed in nitrogen at 700°C for 30 min. During the char preparation, a rapid weight loss (about 65%) occurred in the first 30 min. but the rate of weight loss progressively decreased and an essentially constant rate was attained after about 20 min. The changes that occurred during the initial time on stream are due to volatilization of moisture and other volatile materials from the coal. The constant rate of reaction indicated essentially complete devolatilization, leaving predominantly carbon and the residual inorganic components of the coal that were not removed by the acid leaching.

Figure 18. FT-IR spectra for the coal ion-exchanged with Ca^{2+} using 10^{-1} mol/L $\text{Ca}(\text{NO}_3)_2$ solution. Unloaded coal (A); (B), (C), (D): 1.3, 2.0, 3.2% wt. Ca, respectively.

As can be observed in Figure 19, the conversion of the char derived from the demineralized, unloaded coal increased very slowly with reaction time, reaching a maximum gasification of only about 20 %wt. Char conversion (or burn-off) is defined as the amount of the char reacted in CO_2 as a function of time, expressed as a percentage of the quantity of char at the time the CO_2 is turned on. Since it is well known that some of the inorganic constituents of coal catalyze gasification reactions, the low reaction rate in CO_2 is further indication of the high degree of demineralization.

The activities of the catalysts for char conversion will be compared using the reactions catalyzed by potassium acetate, potassium carbonate, potassium chloride, potassium nitrate and potassium sulfate. The corresponding reactivities for these catalysts are shown in Figures 20-24. Three catalyst loadings, as specified in the figure captions, were investigated for each catalytic salt. The data presented in Figures 20-24 are similar to those obtained for the chars catalyzed by the calcium salts and are therefore not included here. Comparison of Figures 19-24 shows that the reactivities of the chars were, in general, higher at all catalyst loadings than the uncatalyzed char. It is also observed that except for the potassium nitrate catalyzed reaction (Figure 23), the char gasification rates increased with increase in the potassium content of the coal. For example, the maximum char conversions are approximately 25, 45 and 57 %wt for the chars containing 1.26, 3.18 and 3.23 %wt K, respectively, when the potassium carbonate salt was applied. These results are consistent with the zeta potential results which, as discussed earlier, become less negative with increase in quantity of metal catalyst adsorbed. The opposite effect was observed when the maximum char conversions are normalized to reactivities per gram of catalyst (see Table 3, column 4); the reactivities decreased with increase in catalyst loading. The high normalized reactivity of 118.6 %wt. for the 0.59 %wt. potassium loading (with KCl as the catalyst precursor) is attributed to experimental error since the char conversion can not exceed 100 %wt. The decline in char reactivities with increase in catalyst loading can be due to reduction in catalyst dispersion as the catalyst loading is increased and/or to

Figure 19. Reactivity of the unloaded demineralized lignite char in CO₂ at 700°C.

Figure 20. Reactivities in CO_2 at 700°C . of the demineralized lignite chars containing 0.89, 2.34 and 2.93 %wt. potassium, respectively, for (A), (B) and (C). The catalyst precursor was KOOCCH_3 .

Figure 21. Reactivities in CO_2 at 700°C . of the demineralized lignite chars containing 1.26, 3.18 and 3.23 %wt. potassium, respectively, for (A), (B) and (C). The catalyst precursor was K_2CO_3 .

Figure 22. Reactivities in CO_2 at 700°C . of the demineralized lignite chars containing 0.59, 1.75 and 2.61 %wt. potassium, respectively, for (A), (B) and (C). The catalyst precursor was KCl.

Figure 23. Reactivities in CO_2 at 700°C . of the demineralized lignite chars containing 0.82, 1.64 and 2.34 %wt. potassium, respectively, for (A), (B) and (C). The catalyst precursor was KNO_3 .

Figure 24. Reactivities in CO_2 at 700°C . of the demineralized lignite chars containing 1.02, 1.65 and 2.44 %wt. potassium, respectively, for (A), (B) and (C). The catalyst precursor was K_2SO_4 .

the plugging of the coal's pores by the catalysts. The latter phenomenon will limit diffusion of carbon dioxide to the coal's internal pore structure and diffusion of the reaction products from the pores, resulting in the observed decrease in reactivities.

Table 3. Maximum reactivities for the demineralized coal loaded with the various potassium salts

<u>Catalytic Salt</u>	<u>Potassium, %wt.</u>	<u>Burn-off, %wt.</u>	<u>Burn-off, % wt./g cat</u>
KOOCCH ₃	0.89	65	73.0
KOOCCH ₃	2.34	60	25.6
KOOCCH ₃	2.93	58	19.8
K ₂ CO ₃	1.26	21	16.7
K ₂ CO ₃	3.18	42	13.2
K ₂ CO ₃	3.23	55	17.0
KCl	0.59	70	118.6
KCl	1.75	65	37.1
KCl	2.61	75	28.7
KNO ₃	0.82	54	65.9
KNO ₃	1.64	45	27.4
KNO ₃	2.34	59	25.2
K ₂ SO ₄	1.02	30	29.4
K ₂ SO ₄	1.65	45	27.3
K ₂ SO ₄	2.44	55	22.5

Comparison of the normalized char gasification results shows that the chars containing potassium carbonate are relatively less reactive than the chars loaded with the other catalytic salts. This observation can be ascribed to the relatively higher potassium contents of the coals loaded with K_2CO_3 , and the to the possible decrease in catalyst dispersion and mass transfer limitations as discussed above. The potassium carbonate results are in contrast to those reported in the literature which show that the reactivities of chars catalyzed by K_2CO_3 are generally much higher than those for the other catalyst precursors. Table 3 also shows that the gasification rate in the presence of potassium chloride is similar to those of the oxygen-containing catalysts and suggests that the presence of oxygen in the catalyst precursor does not have any significant effect on the activities of the catalysts in this study. The observed reactivities may be better understood from catalyst dispersion results. Unfortunately, coal-catalyst systems are not amenable to the currently available catalyst dispersion measurement techniques.

Kannan and Richards⁷¹ have recently attributed the reactivities of oxygen-containing potassium catalyst precursors to the decomposition of the salts to potassium oxides, such as K_2O , at about 500-600°C. They have postulated that K_2O is subsequently reduced to metallic potassium. Yokoyama et al⁷² have reported that when heated in vacuum at ~650°C, carbon-doped K_2CO_3 is decomposed to K_2O and CO_2 and that the K_2O is further reduced by carbon to elemental potassium. They have proposed that at gasification temperatures above 650°C, the metallic potassium interacts with the aromatic functional groups in the char to produce highly active catalytic species. Although the dependence of gasification activity on catalyst surface area has been reported⁷³, the gasification activities in this work can not be attributed to differences in surface areas because of the low and similar surface areas of the coal samples investigated.⁷³

3.6 Summary and Conclusions

The disparities in the activities of coal gasification catalyst salts containing the same metal but different anions are well known, even though catalytic function is invariably attributed to the metal components. It has been suggested that the differences are due to the presence or absence of oxyanions in the catalyst precursor and that the formation of coal-oxygen-metal bonds are necessary for effective char reaction. However, the influence of the catalytic salts on the surface chemistry of aqueous suspensions of coal has not been studied, despite the preponderance of catalyst loading from solution. The current work has shown that the electrokinetic properties of an acid-leached lignite are modified by various calcium or potassium catalyst precursors, namely, $\text{Ca}(\text{OOCCH}_3)_2$, CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, KOOCCH_3 , KCl , KNO_3 , K_2CO_3 , or K_2SO_4 . The addition of each salt diminished the negative charge density on the coal particles compared to that on the colloidal particles to which no catalyst precursor was added. At the same salt concentration, the extent of charge reduction is more prominent for the calcium- than for the potassium-containing salts. The net negative zeta potential was also decreased by an increase in the concentration of the catalyst precursor. Under similar conditions, the calcium or potassium adsorption varied significantly, although the adsorption data correlate the zeta potential trends. At 10^{-1} mol/L salt concentration, the maximum calcium loading occurred when calcium acetate was used whereas the level of calcium adsorbed from the calcium chloride or the calcium nitrate solution was much lower. The dependence of potassium uptake on potassium salt followed the order: carbonate > acetate > nitrate ~ chloride ~ potassium sulfate. FT-IR spectra show that Ca^{2+} or K^{+} was exchanged for the protons on the coal surface carboxylic acid functionalities.

The current study has shown that the surface charge and the adsorptive properties of North Dakota Hagel lignite and its demineralized derivative are strongly influenced by the coal slurry pH and by the type and concentration of the various catalyst precursors. Consistent with the zeta potential data and the catalyst metal adsorption results, the reactivities of the chars generally increased with increase in catalyst loading. However, when the char conversions are normalized to reactivities per gram of catalyst adsorbed, the gasification rates decreased with increase in catalyst loading. This may be due to catalyst sintering at reaction temperatures, with the attendant greater reduction in catalyst dispersion at the higher catalyst loadings. The observed inverse correlation of reactivity with catalyst content can also arise from pore plugging by the catalysts and the concomitant mass transfer limitations during the gasification reactions. Advancements in analytical techniques for coal, particularly catalyst dispersion measurement techniques, will increase our understanding of the mechanisms of catalytic coal gasification.

3.7 References

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