DOE/PC/91286--T5

DOE/PC/91286--T5

DE93 011624

THE ROLE OF CATALYST PRECURSOR ANIONS IN COAL GASIFICATION

Fifth Quarterly Report

Godfried M.K. Abotsi
Principal Investigator

Research Center for Science and Technology
Clark Atlanta University
Atlanta, GA 30314

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-FG22-91PC91286

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

BP

No Summary

**THE ROLE OF CATALYST PRECURSOR ANIONS
IN COAL GASIFICATION**

Fifth Quarterly Report

**Godfried M.K. Abotsi
Principal Investigator**

**Research Center for Science and Technology
Clark Atlanta University
Atlanta, GA 30314**

**PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-FG22-91PC91286**

ABSTRACT

The aims of the proposed project are to enrich our understanding of the roles of various aqueous soluble catalyst precursor anions on the surface electrical properties of coal and to ascertain the influence of the surface charge on the adsorption, dispersion, and activities of calcium and potassium. These goals will be achieved by impregnating a demineralized North Dakota lignite (PSOC 1482) with calcium or potassium catalyst precursors containing acetate (CH_3COO^-), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}) anions.

Demineralization of the coal has been completed. In the past quarter, the effects of chloride anion on the surface charge properties of the demineralized coal has been studied using calcium or potassium chlorides. Like the compounds investigated previously, increasing anion concentrations produce less negative charge on the coal surface through the interaction of calcium or potassium ions with the surface.

To date, Fourier transform infrared studied aimed at an understanding of the interaction between the metal ions (Ca^{2+} or K^+) and the coal surface oxygen functionality has not been very informative, most probably due to the high infrared absorption by coal. For this reason, we have procured a resin, Amberlite IRC-50, with carboxylic surface functionality (RCOOH , from Rohm and Haas Company) to be used for metal ion adsorption and the FTIR studies. We hope the similarity between the surface functionality on this resin and coal will provide insight on the mechanism of metal uptake by coal.

DISTRIBUTION

Dr. Kamalendu Das
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26505

Marilyn Keane
OM-40, MS922-206
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

John R. Columbia
Contract Specialist
AD-22, 921-165
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

Kay Downey
Office of Technology Transfer
Mail Stop 58-M217
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

INTRODUCTION

Coal gasification activity is generally attributed to the metal components of catalyst precursors. However, there is evidence that the anion of the catalytic salt plays a significant role in the performance of the catalyst. It has been reported (1) that for the same metal, the chlorides, acetates, or hydroxides of sodium, potassium, magnesium, and calcium exhibited different char reactivities. The catalysts were loaded from aqueous solution. For example, 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. The variations in the activities of the catalysts were also ascribed to differences in the extent of deactivation as a result of the catalyst reaction with inorganic materials in the coal, and to the presence or absence of coal surface metal-oxygen complexes which have been hypothesized as essential prerequisites for coal char reactivity (2-7). It has also been suggested that the metal ion of the catalyst salt reacts with the carbon in the char to form active intermediates for gasification and that the anion of the salt favorably modifies the structure of the active species. However, the composition and structure of the active intermediates are unknown (8).

Since coal is normally impregnated with catalyst from solution, the variations in the activities of different catalyst precursors may be due to the influence of different anions during the adsorption of the metal ions onto the coal. The surface charge properties of aqueous suspensions of coal is well known. However, the effects of catalyst precursor anions on coal electrokinetic properties, catalyst adsorption, dispersion and activity have not been determined. The goal of this project is to investigate these parameters in relation to catalyzed coal gasification.

EXPERIMENTAL

The influence of chloride anion on the zeta potentials of the raw coal and its demineralized derivative was determined using the calcium or potassium chloride. The experimental procedure is analogous to that described in a previous report (9).

RESULTS AND DISCUSSION

As reported previously (9), varying effects of anions on the zeta potentials of a North Dakota Lignite were observed when different concentrations of acetate, chloride, carbonate, nitrate, and sulfate anions were applied. The potassium compounds of these anions were used in that study (9). During the foregoing quarter, zeta potential studies were focused on the effects of calcium or potassium chloride on the surface electrochemistry of the raw coal and its demineralized sample. The results in Figure 1A is the zeta potential - pH plot for the raw coal while Figure 1B is that for the acid leached coal without CaCl_2 addition. Figures 1C and 1D show the effects of 0.001 and 0.01 mol/L CaCl_2 on the zeta potentials, respectively. Comparison of Figures 1A and 1B shows that demineralization dramatically increased the negative charge density on the coal relative to that on the raw coal. This phenomenon has been attributed to the conversion of carbonyl groups to carboxyl groups and the resultant dissociation of the latter. It is also observed (Figures 1C and 1D) that addition of calcium chloride to the demineralized coal reduced the negative zeta potential on the coal significantly. At 0.01 mol/L chloride anion (from CaCl_2) concentration, the negative surface charge density is less than that on the raw coal. For instance at $\sim \text{pH } 9.5$, the zeta potential for the parent coal was approximately -60mV while that on the demineralized coal was about twice as much (-120 mV). However, addition of 0.01 mol/L Cl^- reduced the charge density on the acid leached coal to about -15mV. A similar trend is observed when using potassium chloride as the chloride anion source (Figure 2). However, the reduction in negative zeta

potential is much less pronounced in the case of KCl than CaCl_2 at identical chloride anion concentration. Whereas addition of 0.01 mol/L Cl^- (from CaCl_2) reduced the zeta potential on the demineralized coal from -120 mV to -15 mV, the same level of chloride anion content reduced the zeta potential from -120 to -80 mV. These results can be explained by the Schulze - Hardy rule (10) which states that the extent of adsorption of an ionic species is dependent on the charge of the ion and that the degree of adsorption increases with increase in the ionic charge. Since the original coal particles are negatively charged, chloride anion adsorption will be hindered as a result of electrostatic repulsion between the coal surface and the Cl^- anion. Thus, the reduction in surface charge must arise from the adsorption of calcium or potassium ions produced from the dissociation of the chlorides, the driving force for the adsorption being coulombic attraction between the anionic coal surface and the metal ions. The greater effect of the Ca^{2+} on the zeta potential compared to that of the K^+ can be accounted for by the Schulze - Hardy rule.

In conclusion, it has been shown that the negative charge density on a North Dakota lignite and its demineralized derivative is reduced in the presence of KCl and CaCl_2 solutions. For each compound, the reduction becomes more prominent as the salt concentration is increased, the phenomenon being more distinct for CaCl_2 than KCl. The higher reduction in negative zeta potential by the former compound is ascribed to its higher valence which enhances calcium ion adsorption by the coal than potassium ion adsorption.

Because of the high infrared absorption by coal, we have procured a resin (Amberlite IRC-50) which, like coal, has surface carboxylic functional groups but it is light brown in color and should therefore adsorb less infrared radiation. Adsorption and FTIR studies on this model sample are in progress to gain insight into the interaction between the metal ions and oxygen functionality on coal. The effects of various parameters such as coal drying conditions, KBr to coal ratio, instrument purging time,

and number of scans are being investigated to enhance the spectra and facilitate interpretation of the results.

REFERENCES

1. Calahorro, C.V.; Gonzalez, C.F.; Garcia, A.B.; Serrano, V.G., Fuel 1987, 66, 216.
2. Wigmans, T.; Haringa, H.; Moulijn, J.A., Fuel 1983, 62, 185.
3. Hashimoto, K.; Miura, K.; Xu, J. -J.; Watanabe, A.; Masukami, H. Fuel 1986, 65, 489.
4. Wigmans, T.; van Craneburgh, H.; Elfring, R.; Moulijn, J.A., Carbon 1983, 21, 23.
5. Yuh, S.J.; Wolf, E.E., Fuel 1983, 62, 252.
6. Fredriks, I.L.C.; van Wechem, H.M.H.; Stuiver, J.C.M.; Bouwman, R., Fuel 1981, 60, 463.
7. Mims, C.A.; Rose, K.D.; Melchior, M. T.; Pabst, J.K., J. Am. Chem. Soc., 1982, 104, 6886.
8. Wood, B.J. and Sancier, K.M. Catal. Rev. Sci. Eng. 1984, 26(2), 233.
9. Abotsi, G.M.K., "The Role of Catalyst Precursor Anions in Coal Gasification" 3rd Quarterly Report Prepared for Department of Energy, Grant No. DE-FG22-91PC91286.
10. Adamson, A. W., "Physical Chemistry of Surfaces", 5th edn., John Wiley & Sons, New York, 1990, p. 224.

Figure 1. Dependence of zeta potential on coal slurry pH for North Dakota Hagel lignite (PSOC 1482) (A) and its demineralized derivative (B). Effects of 0.01 and 0.001 mol/L chloride anion concentrations, (C) and (D) respectively. Calcium chloride as source of Cl^- .

Figure 2. Dependence of zeta potential on coal slurry pH for North Dakota Hagel lignite (PSOC 1482) (A) and its demineralized derivative (B). (C), (D) and (E): 0.1, 0.01 and 0.001 mol/L chloride anion concentrations, respectively. Potassium chloride as source of Cl^- .

**DATE
FILMED**

5 / 7 / 93