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

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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 North Dakota lignite (PSOC 1482) and its demineralized derivative 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. Catalyst loading will be conducted under well-controlled conditions of solution pH and ionic strength.

In the last quarter, the surface charge properties of the coal was determined as a function of acetate (CH_3COO^-), chloride (Cl^-), nitrate (NO_3^-), carbonate (CO_3^{2-}) or sulfate (SO_4^{2-}) concentration using the respective potassium salts of these anions. In general, low anion concentrations (10^{-3} or 10^{-2} mol/L) had little effect on the zeta potentials of the coals. However, the surface charge densities of the coal become less negative at 10^{-1} mol/L of the nitrate, carbonate or sulfate anions. These trends suggest that the surface charge density of the coal is controlled by the adsorption of potassium ions (K^+) onto the coal particles. The net negative charge on the coal particles creates a repulsive force between the anions and the coal surface and prevents the anions from exerting any significant effect on the coal's electrokinetic properties.

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, and 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 catalysts 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 catalytic 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 catalytic salts of the same metal may be due to the influence of the different catalyst precursor 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 surface electrochemistry of the raw coal (North Dakota Hagel lignite, PSOC 1482) in the presence or absence of acetate (CH_3COO^-), chloride (Cl^-), nitrate (NO_3^-), carbonate (CO_3^{2-}) or sulfate (SO_4^{2-}) anion was investigated by dispersing 300 mg of the coal (-200 mesh sieve size) in a liter of distilled water containing 10^{-1} , 10^{-2} or 10^{-3} mol/L of each anion. The potassium compound of each anion was used as the source of the anion. The slurries were divided into 50.0 ml portions and the pHs were adjusted with a few drops of dilute nitric acid or ammonium hydroxide solution. Ionic strength was controlled with 10^{-3} mol/L sodium nitrate. The slurries were mechanically agitated for 3h to attain equilibrium followed by redetermination of the pHs and the zeta potential measurements using "Pen Kem model 501 Lazer Zee Meter."

RESULTS AND DISCUSSION

The effects of the anion concentrations on the zeta potentials are compared to that of the parent coal in Figures 1-5. As evident, the surface charge density on the coal increases progressively as the pH of the slurry is raised from about pH 2 to 10. This behavior has been attributed to the dissociation of the coal surface carboxylic and hydroxyl groups, as discussed by several investigators (9-11). Notwithstanding some scatter in the data, Figures 1 and 2 show that the addition of various concentrations of the acetate or the chloride ion to the coal generally results in a decrease in the negative surface charge density on the coal. However, the effect of anion concentration on the zeta potential is essentially the same for all the anions investigated. The reduction in the negative charge density is ascribed to the adsorption of potassium cations onto the negatively charged coal surface.

Comparison of Figures 1 and 2 with Figures 3-5 shows that the zeta potential results are similar for the acetate, chloride, carbonate or the sulfate anions at concentrations of 10^{-3} or 10^{-2} mol/L. However, a significant decrease in the negative zeta potential values

are is obtained in the presence of the carbonate and sulfate anions (Figures 3 and 4). This behavior is also observed for the nitrate anion in the pH 6 - 10.5 range. Reasons for this phenomenon are not clear at this moment and further investigations are in progress to elucidate it. Figure 5 shows that the various nitrate concentrations produced more wide spread zeta potentials than all the other anions. These peculiar data will be reinvestigated to confirm or refute the results.

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Figure 1. Dependence of coal zeta potential on pH and acetate anion concentration.

Figure 2. Dependence of coal zeta potential (surface charge) on pH and chloride anion concentration.

Figure 3. Variation of coal zeta potential with pH and carbonate anion concentration.

Figure 4. Variation of coal zeta potential with pH and sulfate anion concentration.

Figure 5. Variation of coal surface charge with pH and nitrate anion concentration.

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