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THE ROLE OF CATALYST PRECURSOR ANIONS IN COAL GASIFICATION

Tenth Quarterly Report

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ABSTRACT

This project investigates the roles of various aqueous soluble catalyst precursors containing various anions, specifically acetate (CH_3COO^-), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}) on the surface electrical properties of coal and seeks to understand the effects of these salts on the adsorption, dispersion and activities of calcium and potassium.

The current report discusses the reactivities the lignite derived char catalyzed by ~0.05 - 0.07 %wt. potassium. The catalytic compounds used were potassium acetate, potassium carbonate, potassium chloride, potassium nitrate, and potassium sulfate. The initial concentration of each salt solution from which potassium was ion-exchanged onto the coal was 0.001 mol/L and the metal was ion-exchanged onto the coal at the approximate pHs of 2, 6 and 9. Although the potassium contents in the chars were similar (~0.05 - 0.07 %wt.), a wide spread of char reactivities were observed. Char gasification ranged from > 90 %wt. to < 20 %wt. At this time, no general correlation between char reactivities, catalyst type, catalyst precursor anions or catalyst loading pH is obvious. However, the data are currently being analyzed in terms of zeta potentials to determine the effects, if any, of the coal surface properties on catalyst dispersion and gasification rate.

INTRODUCTION

Coal gasification activity is generally attributed to the metal component of catalyst precursors. However, there is evidence that the anion of the catalyst 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 of 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 various cations (e.g., Na^+ , K^+ , Mg^{2+} or Ca^{2+} produced by the dissociation of the metal precursors at the gasification temperatures) through pores of the chars. The variations in the activities of the catalysts were also ascribed to differences in the extent of catalyst 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. Although the surface charge properties of aqueous suspensions of coal are well known, 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 SECTION

The effects of the various catalyst precursors on char reactivity were studied in carbon dioxide. A Dupont 951 thermogravimetric analyser, 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 1 h. The reaction was repeated on the coal samples exchanged at pH 9-10 with 10⁻³ mol/L of potassium acetate, potassium nitrate, potassium chloride, potassium carbonate and potassium sulfate.

RESULTS AND DISCUSSION

The behavior of the unloaded acid-leached coal during the char preparation and its reaction in carbon dioxide has been discussed previously (9). As reported in an earlier report and shown here in Figure 1, the potassium uptake from all the 10⁻³ mol/L potassium salt solutions occurred within a narrow range (~0.5 - 0.7% wt.). It can be seen from Figures 2-6, that significant variations occur in the char gasification rates for these potassium compounds although the metal contents of the coals are similar. Char reaction was conducted for ~ 1 h and the gasification rates shown in Figures 2-6 are for reaction times of 0, 5, 25 and 50 min. It is observed from Figure 2 that the highest char gasification rate was obtained when potassium (0.07 %wt.) was loaded onto the coal at pH 2.1. Although the potassium content is essentially the same as those obtained when the metal was exchanged at pH 6.5 and 9.3 (0.10 and 0.07 %wt. K, respectively), the reactivities of the latter samples are significantly less. Whereas the most reactive specimen has a maximum gasification rate of ~93 %wt. for the KCl (pH 2.1) catalyzed sample, the highest

reaction rates for potassium acetate (Figure 3) and potassium nitrate (Figure 4) are only about 40 %wt. Unlike potassium chloride, maximum gasification rates for the latter two compounds occurred at pH 4.5 and pH 9.0, respectively. In the case of potassium sulfate, the most reactive char was that obtained from catalyst loading at pH 5.3. A substantial difference in char reactivity is also observed for the catalysts loaded at this pH and those exchanged onto the coal at pH 2 or pH 8.9, even though the potassium contents are very similar. Unlike previous literature reports which generally show comparatively high gasification rates for potassium carbonate, the current study indicates that at low potassium carbonate loadings of ~0.5-0.7 %wt., the char reactivities are significantly lower than those of potassium acetate, potassium chloride, potassium nitrate or potassium sulfate.

Coal-oxygen-metal (C-O-M) complexes have been hypothesized as essential prerequisites for char reactivity (2-7). It has been shown that high initial gasification activities were obtained for oxygen-containing potassium or sodium salts (K_2CO_3 , KNO_3 , KOH , K_2SO_4 and Na_2CO_3) used to load carbon. 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 bonds. Kannan and Richards (10) 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 al (11) 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, metallic potassium interacts with the aromatic functional groups in the char to produce highly active catalytic species. The high reactivity of the KCl -loaded samples in this report contradicts the earlier reports and further work is suggested to test the role of oxygen and other atoms such as chlorine in coal gasification. The dependence of gasification activity

on catalyst surface area has been observed by Delacea and co-workers (12). However, in this work, the surface areas are relatively small ($0.5 - 1 \text{ m}^2 \text{ g}^{-1}$) and similar and therefore not play a significant role in the gasification reaction.

Since the potassium contents are similar for the coal samples in the current study, it is suggested that the differences in the char reactivities are linked to the various anions in the catalyst precursors. However, the specific functions of the anions in the gasification reactions are unknown. Catalyst dispersion measurements may be useful in explaining the variations in char gasification rates observed in the this study. Considering the difficulty in determining catalyst dispersion in a rather heterogeneous material as coal, it will be beneficial to utilize a less complex substance -- carbon as a substrate onto which the catalyst precursors can be adsorbed and used for evaluating catalyst dispersion.

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Figure 1. Potassium adsorbed from various potassium salt solutions (10^{-3} mol/L) as a function of solution pH.

Figure 2. Char reactivity in CO_2 at 700°C with potassium chloride as the catalyst precursor.

Figure 3. Char reactivity in CO₂ at 700°C with potassium acetate as the catalyst precursor.

Figure 4. Char reactivity in CO₂ at 700°C with potassium nitrate as the catalyst precursor.

Figure 5. Char reactivity in CO₂ at 700°C with potassium sulfate as the catalyst precursor.

Figure 6. Char reactivity in CO₂ at 700°C with potassium carbonate as the catalyst precursor.

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