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THE ROLE OF CATALYST PRECURSOR ANIONS IN COAL GASIFICATION

Eighth Quarterly Report

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ABSTRACT

This project investigates the roles of various aqueous soluble catalyst precursor anions, specifically acetate (CH_3COO^-), chloride

(Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}) anions on the surface electrical properties of coal and seeks to understand the effects of these anions on the adsorption, dispersion and activities of calcium and potassium.

The effects of the various anions on coal char gasification is currently under investigation. The influence of acetate, chloride and nitrate ions, when using the corresponding potassium compounds, are discussed in this report. The thermograms for the char preparation in nitrogen show that rapid devolatilization (~65 %wt.) of moisture and other volatile materials occurs in the first 30 min. The rate of weight loss decreases significantly thereafter up to about 70 min. when char preparation was complete.

Introduction of carbon dioxide after this time resulted in only a small amount (8 %wt.) of carbon gasification of the unloaded, demineralized coal. However, the chars containing the acetate, chloride or nitrate of potassium gave reactivities of 24.8, 30.4 or 24.3 %wt., respectively. The catalysts were ion-exchanged with the salt solutions and the corresponding potassium contents were 2.9, 2.6 and 2.3 %wt. The higher reactivities of the catalyzed chars compared to the unloaded char correlates the high degree of demineralization and the resultant low catalytic activity by the inherent inorganic materials. It is observed that the potassium acetate and the potassium nitrate have similar reactivities, while the reactivity in the presence of KCl is higher. This finding contrasts some of the previous literature reports which show that oxygen-containing catalytic salts are more active catalysts due to the formation of carbon-oxygen-metal bonds which have been postulated as pre-requisites to carbon gasification. The data obtained to date are in agreement with other reports which show that catalytic activity is influenced by other catalyst variables, such as catalyst surface area and not anion type alone.

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

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 20mg 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 1h. The reaction was repeated on the coal samples exchanged at pH 9-10 with 10⁻¹ mol/L of potassium acetate, potassium nitrate or potassium chloride. The time of CO₂ introduction is indicated by arrows in Figures 1-4 and discussed below.

RESULTS AND DISCUSSION

The behavior of the coal during the char preparation and its reaction in carbon dioxide is shown in Figure 1. A rapid weight loss (about 65%) occurred in the first 30 min. but the rate of weight loss progressively decreased thereafter. The changes that occurred during the initial time on stream are due to devolatilization of moisture and other volatile materials from the coal. The reduction in the rate of weight loss denotes essentially complete devolatilization, leaving predominantly carbon and the residual inorganic components of the coal that were not removed by the acid leaching.

As can be observed in Figure 1, introduction of CO₂ had very little effect on the slope of the thermogram. This indicates very low gasification (8 %wt.) in the presence of carbon dioxide. It also confirms the high degree of coal demineralization. It is well known that some of the inorganic constituents of coal catalyze gasification reactions and the low reaction rate in CO₂ is further confirmation of the high degree of demineralization.

The reactivities of the samples loaded with potassium acetate, potassium chloride and potassium nitrate are shown in Figures 2-4. As can be observed from these Figures, the thermograms for char preparation are similar to that obtained for the unloaded coal. However, beyond ~70 min., significant CO₂ gasification occurred compared to that of the demineralized coal. At the end of the carbon dioxide reaction time, the amounts of char gasified were 24.8, 30.4 and 24.3 %wt. for the KOOCCH₃, KCl and KNO₃, respectively. The corresponding potassium content of the coal specimens are 2.9, 2.6 and 2.3% wt. K. Thus, the level of reactivity is not significantly different for the various samples. However, the reaction rate in the presence of each catalyst is approximately three times higher than in the absence of added catalyst. It is observed that the reaction rate is higher (30.4% wt.) when KCl was used as the catalytic compound than for KOOCCH₃ or KNO₃. This observation contrasts with some of the previous literature reports which have shown that oxygen-containing catalyst precursors have higher reactivities than those without oxygen (e.g., KCl). The higher reactivities have been attributed to the formation of carbon-oxygen-metal surface complexes which have been hypothesized as pre-requisites for char gasification.

Kannan and Richards (9) have recently attributed the reactivities of oxygen-containing potassium catalyst precursors to the decomposition of the salts to potassium oxides, such as K₂O, at about 500-600°C. They have postulated that K₂O is subsequently reduced to metallic potassium. Yokoyama et al (10) have reported that when heated in vacuum at ~650°C, carbon-doped K₂CO₃ is decomposed to K₂O and CO₂ and that the K₂O 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. The dependence of gasification activity on catalyst surface area has been observed by Delacea and co-workers (11). Thus, the catalytic activities of different salts containing the same metal may be influenced by various parameters.

The reactivities of the coal chars in CO₂, catalyzed by the other catalytic compounds, are currently being investigated and will be discussed in future reports.

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, 462.
7. Mims, C. A., Rose, K. D., Melchoir, M. T., Pabst, J. K., J. Am. Chem. Soc. 1982, 104, 6886.
8. Wood, B. J., Sancier, K. M., J. Catal. Rev.-Sci. Eng. 1984, 26(2), 233.
9. Kannan, M. P., Richards, G. N., Fuel 1990, 69, 999.
10. Yokoyama, S., Tanaka, K., Toyoshima, I., Chem. Lett. 1980, 559.
11. Delecea, C. S. M., Alarcon, M. M., Solano, A. L., Fuel 1990, 69, 21.

Figure 1. Reactivity of the demineralized lignite char in CO₂ at 700°C. Char preparation was conducted in nitrogen for times less than ~70 min. Arrow indicates time of CO₂ introduction.

Figure 2. Char reactivity in CO_2 with potassium acetate as the catalyst precursor. Potassium content = 2.9% wt. See other legend in Fig. 1.

Figure 3. Char reactivity in CO₂ with potassium chloride as the catalyst precursor. Potassium content = 2.6% wt. See other legend in Fig. 1.

Figure 4. Char reactivity in CO_2 with potassium nitrate as the catalyst precursor. Potassium content = 2.3% wt. See other legend in Fig. 1.

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