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THE ROLE OF CATALYST PRECURSOR ANIONS IN COAL GASIFICATION

Seventh Quarterly Report

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Prepared For
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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.

In order to investigate the effects of lower anion concentration on calcium or potassium adsorption, aqueous solutions containing 10^{-3} mol/L of each anion and calcium or potassium were agitated with the acid-leached coal following previously described procedure. Chemical analysis for calcium or potassium shows that metal uptake is substantially reduced compared to metal adsorption from solutions containing higher (10^{-1} mol/L) anion, and hence metal, concentration. For the lower anion content and for the corresponding potassium salts, calcium adsorption is slightly higher at all the pHs investigated than potassium uptake. While calcium loading also increased slightly with increase in pH, the potassium content of the exchanged coals was essentially the same for all the potassium compounds.

FT-IR studies on the unloaded and the calcium or potassium (using $\text{Ca}(\text{NO}_3)_2$ or KNO_3) exchanged coals gave similar spectra. The spectra were obtained for the coal which had previously been ion-exchanged with the calcium or potassium solutions containing 10^{-1} mol/L NO_3^- . In all cases, the adsorption peak $\sim 1700\text{ cm}^{-1}$ which is characteristic for carboxylic acid functional group progressively decreased in intensity as the calcium or potassium content of the coal increased. The remarkable similarity in the spectra for the calcium or potassium loaded coals supports our earlier suggestion that the adsorption mechanism was similar for both metals. Based on zeta potential and adsorption data reported earlier, metal uptake is predominantly controlled by electrostatic attraction between calcium or potassium ions and the negatively charged coal surface.

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 influence of various anions and the zeta potentials of the demineralized coal on the adsorption of calcium or potassium was determined using the calcium or potassium compounds under investigation. The experimental procedure is analogous to that described in a previous report (9), except that the concentration of each anion in this case is 10^{-3} mol/L.

Fourier transform infrared analysis of the acid-leached coal loaded with calcium or potassium nitrate (using 10^{-1} mol/L NO_3^- concentration) or the unloaded coal has been completed. Samples for the FTIR studies were prepared by dispersing ~5 mg of the coal or the catalyst-containing coal in 300 mg of KBr, mechanically vibrating the mixture for 20-30 seconds, followed by drying under vacuum (~333K) prior to recording the spectra.

RESULTS AND DISCUSSION

The adsorption results shown in Table 1 indicate that calcium adsorption is slightly higher than for potassium loading at all the pHs investigated. This observation has been ascribed to divalent nature of calcium, which enhances its coulombic interaction with the negatively charged coal surface, in contrast to the monovalent potassium ion. It is also noticed that calcium uptake increased slightly with increase in the pHs of the coal slurries, consistent with increasing coal surface charge with increase in pH. In contrast to the behavior for calcium, potassium adsorption was minimal (~ 0.07% wt.) and similar at all pHs. As shown in the last report, calcium or potassium adsorption was much higher when 10^{-1} mol/L ion concentration was used. Thus the quantity of metal adsorbed is controlled by both the initial metal ion concentration and the electrokinetic properties of the coal.

TABLE 1.
Calcium or potassium uptake by the demineralized lignite

<u>Catalyst Precursor</u>	<u>Equilibrium pH</u>	<u>Metal loading, % wt.</u>
CaCl ₂	2.1	0.83
CaCl ₂	5.2	1.29
CaCl ₂	9.7	1.12
Ca(OOCCH ₃) ₂	1.9	0.31
Ca(OOCCH ₃) ₂	8.2	0.82
Ca(OOCCH ₃) ₂	10.1	1.01
Ca(NO ₃) ₂	1.9	0.18
Ca(NO ₃) ₂	8.4	0.93
Ca(NO ₃) ₂	10.1	1.00
KCl	2.0	<0.07
KCl	8.2	0.10
KCl	10.0	0.073
KOOCCH ₃	1.8	<0.05
KOOCCH ₃	4.5	<0.07
KOOCCH ₃	9.4	<0.07
KNO ₃	2.1	<0.07
KNO ₃	5.4	0.060
KNO ₃	9.0	0.055
K ₂ CO ₃	2.1	0.059
K ₂ CO ₃	6.0	<0.05
K ₂ CO ₃	9.1	0.057
K ₂ SO ₄	2.0	<0.07
K ₂ SO ₄	5.3	0.063
K ₂ SO ₄	8.9	<0.07

The FT-IR spectra for the calcium- and potassium-containing coals are shown in Figures 1 and 2, respectively. In either case, spectrum A is for the demineralized coal without added metal, while spectra B, C and D are for the coal which has been ion-exchanged with calcium or potassium at about pH 1, 6 or 10, respectively. Both figures show that the spectra are remarkably similar and strongly suggest a similar adsorption mechanism for the calcium and potassium. The peaks around $1600\text{-}1700\text{ cm}^{-1}$ have been assigned to carboxylic acid groups (10). The unloaded coal has a distinct shoulder at $\sim 1700\text{ cm}^{-1}$ but this peak progressively disappears as the calcium or potassium content of the coal is increased by raising the pH of the coal slurries. The metals (Ca or K) content of the coal has been provided in a previous report (9). The dramatic reduction in peak intensity at pH 10 is consistent with the high metal content of the coal at this pH and indicates a greater interaction of the hydroxyl portion of the carboxylic acid functional group with the calcium or potassium ion.

Coal char gasification in carbon dioxide at 700°C has been initiated and will progress through the current quarter.

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Figure 1. FT-IR spectra for the unloaded coal and the coal ion-exchanged with calcium at about pH 1, 6 or 10. A progressive decrease in peak intensity with increase in pH is observed around 1700 cm⁻¹.

Figure 2. FT-IR spectra for the unloaded coal and the coal ion-exchanged with potassium at about pH 1, 6 or 10. A progressive decrease in peak intensity with increase in pH is observed around 1700 cm^{-1} .

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