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A NOVEL APPROACH TO HIGHLY DISPERSING CATALYTIC MATERIALS IN COAL FOR GASIFICATION

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Godfried M.K. Abotsi and Kofi B. Bota
Principal Investigators

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

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Pittsburgh, PA 15236

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ABSTRACT

This project seeks to develop a technique, based on coal surface properties, for highly dispersing catalysts in coal for gasification and to investigate the potential of using potassium carbonate and calcium acetate mixtures as catalyst for coal gasification. The lower cost and high catalytic activity of the latter compound will produce economic benefits by reducing the amount of K_2CO_3 required for high coal char reactivities.

The effects of potassium impregnation conditions (pH and coal surface charge) on the reactivities, in carbon dioxide, of chars derived from demineralized lignite, subbituminous and bituminous coals have been determined. Impregnation of the acid-leached coal with potassium from strongly acidic solutions resulted in initial slow char reactivity which progressively increased with reaction time. Higher reactivities were obtained for catalyst (potassium) loaded at pH 6 or 10. The dependence of char gasification rates on catalyst addition pH increased in the order: pH 6 ~ pH 10 >> pH 1.

INTRODUCTION

Catalyzed coal gasification requires the adsorption of the catalyst precursor onto the coal surface as the first step in a series of consecutive reactions. Previous studies (1) have shown that char reactivities are dependent on the catalyst precursor and the method applied to load the coal with the catalyst. This report is part of ongoing research aimed at understanding the roles of coal surface charge and the pHs of catalyst impregnating solutions on the adsorption and activities of calcium acetate and potassium carbonate. As reported previously (2), the reactivities of chars derived from a lignite, subbituminous, and bituminous coals are strongly dependent upon the coal surface charge and the pHs at which calcium was adsorbed onto the coal. The current report discusses the reactivities of the demineralized coals in carbon dioxide, catalyzed by potassium.

EXPERIMENTAL

The chemical composition of the coals and the procedure for the particle electrokinetic measurements have been described earlier (2). The catalytic activities of the inherent inorganic materials were minimized by demineralization of the coals by treatment in HF and HNO₃ solutions prior to use. Potassium was adsorbed at pH 1, 6 or 10 by mechanically agitating 50.0 cm³ of 5x10⁻² moles l⁻¹ solutions of K⁺ (using potassium carbonate) with 1.0 g samples of the coals for 24h. The pHs of the slurries were adjusted with nitric acid or ammonium hydroxide solutions. Potassium adsorption was determined by both chemical analysis (by Galbraith Laboratories) of the filtered solids and of the filtrates using atomic absorption spectrophotometry.

The potassium- loaded coals were pyrolyzed by heating (at $20^{\circ}\text{C min}^{-1}$) to 800°C in nitrogen ($100\text{ cm}^3\text{ min}^{-1}$) and holding at this temperature for 0.5h. The N_2 supply was then switched off, CO_2 was introduced at the same flow rate, and char reactivity was conducted at 800°C for about 2h.

RESULTS AND DISCUSSION

Table 1 shows that, in general, potassium adsorption onto the demineralized coals increased with increase in the pHs of the coal slurries. The deviations from the pH values were $\pm \text{pH } 0.2$, $\pm \text{pH } 0.5$, $\pm \text{pH } 0.2$ for potassium adsorption at pH 1, pH 6 and pH 10, respectively. It can be seen that the differences in the potassium content of the coals is less pronounced at pH 6 or 10. The similar potassium adsorption values at these pHs implies that coulombic attraction of the potassium ion onto the coal surface is not significantly increased by raising the coal slurry pH, and hence the net negative surface charge densities, of the coals. As reported previously (3), unlike potassium, calcium uptake approximately doubled by increasing the pHs of the coal dispersions from pH 6 to 10. The increased calcium loading is attributed to the divalent nature of the calcium ion (Ca^{2+}) which promotes electrostatic attraction between Ca^{2+} and the anionic coal surface in accordance with the Schulze- Hardy rule (4) which states that the extent of adsorption of an ionic species is directly related to the magnitude of the ionic charge on the adsorbate. The adsorption trends correlate the zeta potentials of the coal particles which become more negatively charged with increase in the pHs of the coal dispersions. The zeta potentials ranged from about -10 mV at pH 1 to about -110 mV at pH 10 (3). This indicates that electrostatic attraction between the potassium ions (K^+) and the negatively charged surface is the dominant driving force for adsorption.

Table 1. Dependence of calcium adsorption on catalyst loading pH.

Demineralized Coal	Metal	Potassium content, % wt.		
		pH 1	pH 6	pH 10
Lignite	K	0.4	2.0	2.1
Subbituminous	K	0.2	1.9	2.6
Bituminous	K	0.2	3.5	2.3

The amounts of carbon burn-off as a function of reaction time for the demineralized potassium-loaded chars are shown in Figures 1-3 for the lignite, subbituminous and bituminous coals, respectively. The calcium catalyzed gasification activities have been reported previously (5). A striking difference between Figures 1, 2 and 3 is that potassium addition to the lignite at pH 1 produced a prominently higher gasification rates than potassium introduction into the subbituminous and the bituminous coals at the same pH. In fact, above 95 min. of reaction, the pH 1 char became more reactive than both the pH 6 or 10 samples. Repeated experiments with different samples of the coal loaded with potassium at pH 1 gave similar results. Thus, this finding can not be attributed to experimental artifacts. Reasons for this peculiar behavior are not clear, but it is possible that for this coal, very high initial potassium dispersion occurred at 0.4% wt. K and that this level of dispersion was maintained as the reaction progressed. In contrast, it appears that the dispersion of the potassium catalysts loaded at pH 6 or 10 decreased with reaction time as evidenced by the constant reactivities after about 25-50 min. on stream.

The reactivities of the demineralized chars in the presence of calcium and potassium are compared in Table 1. Reactivities were obtained using the equation (6):

$$R = \frac{1}{\omega} \frac{dw}{dt}$$

(1)

where ω is the initial weight of char (dry, ash-free) and dw/dt is the rate of char gasification at 1.5 h.

Table 1

Reactivities of the Calcium- or Potassium- Exchanged Coals as a Function of Catalyst Loading pH and Metal Content

Demineralized Coal	pH	Metal adsorbed, % wt.		Reactivity, h^{-1}
		Ca	K	
Lignite	1	0.3		0.28
	6	4.3		0.44
	10	7.2		0.33
	1		0.4	0.54
	6		2.0	0.49
	10		2.1	0.52
Subbituminous	1	0.2		0.16
	6	2.9		0.31
	10	7.8		0.25
	1		0.2	0.18
	6		1.9	0.72
	10		2.6	0.60
Bituminous	1	0.1		0.06
	6	3.3		0.23
	10	5.9		0.25
	1		0.2	0.17
	6		3.5	0.47
	10		2.3	0.30

Figures 1-3 and Table 1 show that potassium is a more effective gasification catalyst than calcium, the maximum char reactivities being $0.72 h^{-1}$ and $0.44 h^{-1}$ for potassium and calcium, respectively. For all the coals, high calcium loadings (5.9, 7.2

and 7.8% wt.) at pH 10 produced lower gasification rates compared to the lower calcium additions (2.9, 3.3 and 4.3% wt. Ca) at pH 6 (5). The reduced activities could be due to pore plugging by the high amounts of calcium which inhibits access of CO₂ to the pores of the chars and/or to reduced catalyst dispersion at the higher calcium loadings. Examination of the calcium-containing coals by x-ray diffraction using CuK α radiation gave diffraction peaks characteristic of CaO (7) for the samples loaded at pH 10 whereas no reflections above the background of the coals were obtained for catalyst addition at the lower pH values. The absence of diffraction peaks has been attributed to high calcium dispersion while their presence is indicative of reduced catalyst dispersion and the concomitant lower activity at pH 10.

Hippo et. al. (6,8) have shown that the reactivities of Darco seam, Texas lignite chars in carbon dioxide and in steam at 650°C progressively increased with increase in the calcium content (which ranged from 1.1 to 12.9% wt. Ca) of the chars. Unlike the current work, calcium was exchanged onto chars which have been previously prepared in N₂ at 800°C. In addition, these investigators did not observe any dependence of char burn-off on calcium adsorption pH from their "limited results obtained" and there were no indications of the pHs of the coal slurries. However, Hengel and Walker (9) have shown that calcium loadings greater than 4% wt. resulted in no further increase in the CO₂ reactivities at 755°C of chars derived from a demineralized Montana (Fort Union seam) lignite. Recently, similar findings have been reported for the CO₂ gasification (at 775°C) of polymer derived carbons onto which various levels of calcium (0.5-9.5% wt. Ca) have been ion-exchanged (10). Since similar N₂ and CO₂ surface areas were obtained for the carbons used in the latter study, the differences in reactivities can not be attributed to differences in the surface areas of the carbons. CO₂ surface area measurements on samples of the demineralized bituminous coal loaded with calcium or potassium at pH 1, 6 or 10 gave

similar values ($\sim 11\text{-}20\text{ m}^2\text{ g}^{-1}$), suggesting that the reactivities are independent of surface area.

CONCLUSIONS

The influence of measured coal surface charge on the adsorption of calcium or potassium from solution prior to gasification has been investigated. The study focused on the demineralized derivatives of three ranks of coal: a lignite, subbituminous and bituminous coals and their demineralized derivatives. To minimize the interference of the coals inherent inorganic materials with the added calcium or potassium, the metal adsorption and gasification studies were restricted to the demineralized (DEM) coals. Potassium was ion-exchanged onto the DEM samples at about pH 1, pH 6 and pH 10. In strongly acidic environments ($\sim$ pH 1), potassium uptake was very low (0.2 - 0.4% wt.), suggesting minimal electrostatic attraction between the cations and the slightly negatively charged coal surface. However, potassium adsorption increased dramatically as the pHs of the slurries were raised to pH 6 or 10. Potassium uptake followed the order: pH 6 $\sim$ pH 10 $\gg$ pH 1, the average potassium concentration in the coals being 0.2% wt. K and 2.5% wt. K at pH 1 and pH 6, respectively.

The reactivities of the potassium-containing chars in CO_2 at 800°C were also strongly dependent on the pHs at which the metals were exchanged onto the coals. Char reactivities in the presence of potassium followed the trend pH 6 $\sim$ pH 10 $\gg$ pH 1, consistent with the potassium contents. This work also shows that when ion-exchanged at pH 6 or 10, potassium is a very active catalyst for the CO_2 gasification of demineralized samples of a North Dakota lignite, Montana subbituminous and Illinois No. 6 bituminous coals and that char reactivities are dependent on the pH, and hence, on the magnitude of the negative surface charge densities on the coals during catalyst loading from solution.

In the next quarter, the effects of co-adsorption of calcium and potassium and the surface areas of the coals on char reactivity will be evaluated.

HIGHLIGHT ACCOMPLISHMENTS, ARTICLES AND PRESENTATIONS

Publications and presentations resulting from this work to date are provided below.

1. Abotsi, G.M.K., Bota, K.B., Gautam Saha, "The Influence of Coal Surface Chemistry on the Adsorption of Coal Conversion Catalysts," Am. Chem. Soc., Div. Fuel Chem. Preprs. 1990, 35(3), 606-610.
2. Abotsi, G.M.K., Bota, K.B. and Gautam Saha, "Electrophoresis as an Aid to Improved Catalyst Dispersion in Coal," 17th Annual National Conference of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, 1990, Abstracts, p. 77.
3. Abotsi, G.M.K., Bota, K.B., Saha, G., "Relationships Between Coal Surface Chemistry, Catalyst Adsorption, and Char Reactivity," American Carbon Society, 20th Biennial Conference on Carbon, Extended Abstracts, 460-461, 1991.
4. Abotsi, G.M.K., Bota, K.B., Saha, G., "Enhancement of Coal Gasification Activity by Coal-Catalyst Interactions," International Energy Agency, International Conference on Coal Science Proceedings, 412-415, 1991.
5. Abotsi, G.M.K., Bota, K.B., Saha, G., "Effects of Coal Surface Charge on the Adsorption and Gasification Activities of Calcium and Potassium," Submitted to Fuel Science & Technology International.

The effects of measured coal surface charge on the adsorption of coal gasification metal catalysts has not been studied previously. This work has shown that the adsorption of calcium or potassium ions onto coals is primarily controlled by the surface charge properties of coal. Coal loading (by ion-exchange) of Ca^{2+} or K^{+} at high pHs which promote the formation of negatively charged coal surface enhanced coulombic attraction between the metal ions and the coal surface with a resultant enhancement of char reactivity. However, char reactivity is reduced by catalyst

addition from strongly acidic solution due to the minimal electrostatic attraction between the cations and the reduced net negative charge on the coal surface.

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Figure 1. Reactivities of the demineralized, unloaded lignite char (DEM 1482) and the demineralized chars loaded with potassium at pH 1, pH 6 and pH 10. Char reactivities were conducted in carbon dioxide at 800°C for about 2h.

Figure 2. Reactivities of the demineralized unloaded (DEM 1485) char derived from the subbituminous coal (PSOC 1485) and of acid-leached coals loaded with potassium at pH 1, pH 6 and pH 10. Char reactivities were performed in CO_2 at 800°C for $\sim 2\text{h}$.

Figure 3. Dependence of char reactivities on potassium loading pH for the demineralized Illinois No. 6 coal. DEM 1493 denotes the unloaded demineralized coal; potassium loading pHs are indicated by arrows. Reaction was carried out in CO_2 at 800°C .

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