

# ASSESSMENT OF CATALYST-CONTAINING COAL-WATER SLURRY FORMULATIONS

G. Saha, K. B. Bota and G. M. K. Abotsi

Department of Chemistry  
Clark Atlanta University  
Atlanta, GA 30314

## INTRODUCTION

The aim of this work is to investigate the preparation of iron-containing coal water slurries for coal liquefaction or gasification. The low cost of iron-based catalysts makes them attractive as disposable catalysts. Various iron compounds such as iron sulfate, pyrite, ferrous sulfide, and hydrated iron oxide have been used for coal liquefaction (1,2). Pyrrhotite is generally believed to be the active liquefaction catalyst which is formed from pyrite or by reaction of iron compounds with added elemental sulfur or with hydrogen sulfide either introduced into the reactor or generated by coal desulfurization during liquefaction (3,4).

Wender et al (5,6) have reported improved liquefaction activities of sulfated iron oxide ( $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ ), tin oxide ( $\text{SnO}_2/\text{SO}_4^{2-}$ ), and the bimetallic catalyst  $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ . It was suggested that the sulfate group increases catalyst dispersion by inhibiting the agglomeration of the metal oxide catalysts at high temperatures. Thus, it will be useful to investigate the effects of sulfate ions on the dispersion and activity of iron in coal-water slurries. A greater insight into the role of the sulfate ion in the catalysis of coal hydrogenation can lead to the formulation of more active catalysts.

Iron catalysts, particularly mixtures of iron and alkali metal catalysts, have also been shown to be active for coal gasification. Huttinger and Minges (7) suggested that iron catalyses the reduction of alkali salts to the metals, the main catalytic species for gasification. In general, iron catalysts loaded from aqueous solution are more active for coal conversion than those physically mixed with coal (1). The enhancement in activity has been attributed to higher catalyst dispersion resulting from better contact between the catalyst precursor and the coal surface.

The formulation of coal-water slurries as fuels in power plants has been the subject of many investigations (8). However, catalyst-containing coal-water slurries intended for coal liquefaction or gasification have received little research attention, although efficient catalyst adsorption and dispersion in the coal can be expected during the long-distance

transportation of the fuels to the coal gasification or liquefaction unit. This work evaluates the uptake of iron by coal particles dispersed in water. Since surfactants are used to increase the dispersion and stability of coal-water slurries, the effect of sodium dodecylsulfate (SDS), a surfactant, on the loading of iron onto Illinois No. 6 coal (DECS-24) was investigated.

## EXPERIMENTAL

The coal was supplied by the Penn State Coal Sample Bank. Its moisture, ash, volatile matter, and fixed carbon contents were 13.2, 11.6, 35.4, and 39.7 %wt., respectively, on as-received basis. It has an ultimate analysis (as-received) of 11.6 % ash, 57.3 % carbon, 4.0 % hydrogen, 1.0 % nitrogen, 4.8 % sulfur, and 8.1 %wt. oxygen (by difference).

Coal-water slurries were prepared by weighing 2.0 g of the coal into 250 mL flasks, followed by addition of 25 mL of  $10^{-2}$ ,  $10^{-3}$  or  $10^{-4}$  mol/L SDS solution prepared using deionized water. Control studies, without added SDS, were also conducted. The samples were mechanically agitated for 3, 6, 9 or 15 hours to effect the adsorption of the surfactant onto the coal particles. At the end of the adsorption time, 25 mL of  $10^{-2}$  mol/L Fe solution, using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , were added to each slurry and mechanically shaken for 24 hours to allow iron uptake by the coal. The pH of each slurry was measured after the adsorption experiments. Following the iron adsorption, the coal residues were filtered, dried, and analyzed for iron by Galbraith Laboratories, Knoxville, TN.

## RESULTS AND DISCUSSION

The iron uptake onto the SDS treated and untreated coal is shown in Figure 1. In general, iron loading increased with adsorption time. It is observed that the highest iron uptake occurred between 3 and 9 hours for the sample containing the highest SDS concentration. Within the same time interval, addition of 0.5 or 0.05 mMol of SDS produced lower iron loading compared to the samples which were not treated with SDS. Previous studies (9) have shown that iron adsorption onto coal occurs through exchange of the cation ( $\text{Fe}^{2+}$ ) with the protons on the carboxylic or phenolic acid groups on coal. This

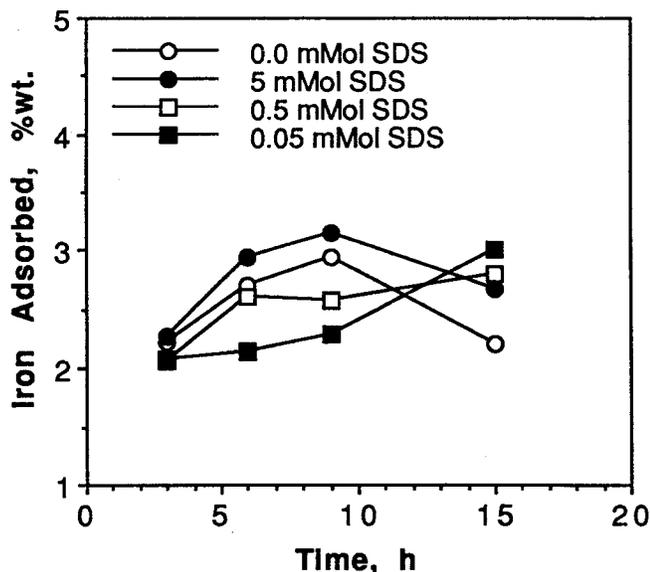
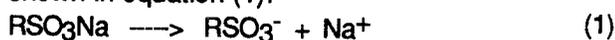


Figure 1. Iron adsorption onto the parent and the SDS treated coal.

was confirmed by FT-IR studies (9). Thus, iron loading onto the coal in the absence of SDS can be attributed to exchange of the metal ion with the protons on the oxygenated surface functionality.

The zeta potential results in Figure 2 show that the coal surface is negatively charged and has a zeta potential of about -40 mV at ~pH 4.2, the average pH for the SDS treated and untreated coal slurries. The increase in the negative zeta potential with increase in pH is attributed to the dissociation of the surface carboxylic and phenolic acid groups and hydroxylated metal oxides which create negative charge on the surface. The dissociation is most pronounced in basic media. In aqueous solution, SDS will dissociate to produce an anion and  $\text{Na}^+$  as shown in equation (1):



where R denotes the organic portion of the surfactant. Since the coal surface is negatively charged, the anionic polar group of the surfactant will be repelled from the solid surface. Hence, SDS will be adsorbed onto the coal surface through hydrophobic interaction of the organic portion of the anion with the hydrophobic sites on the coal, with the negative polar group oriented towards the aqueous phase (10). This will favor  $\text{Fe}^{2+}$  adsorption through electrostatic interaction between  $\text{Fe}^{2+}$  and the negative polar sites.

In conclusion, work to date has shown that iron adsorption onto Illinois No. 6 coal (DECS-24) is promoted by coal pretreatment with  $10^{-2}$  mol/L of sodium dodecylsulfate, while iron uptake is reduced by lower surfactant concentration. Subsequent

studies will focus on the rheological properties of the coal-water slurries and their liquefaction and gasification behavior.

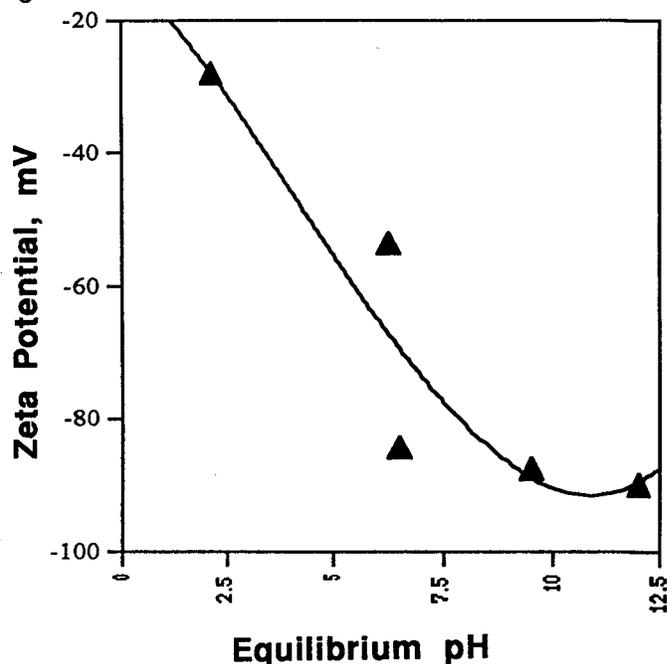


Figure 2. Zeta Potential of the parent coal as a function of slurry pH.

#### ACKNOWLEDGEMENT

This study was funded by the Department of Energy, Grant No. DE-FG22-91PC91286.

#### REFERENCES

1. E. E. Donath and M. Hoering, *Fuel Proc. Tech.*, **1** 3 (1977).
2. K. Tanabe et al., *Fuel Proc. Tech.*, **14** 247 (1986).
3. Y. Kamiya et al., *Fuel Proc. Tech.* **18** 1 (1988).
4. Wurfel, H. E., *Fuel Proc. Tech.* **2** 227 (1979).
5. V. R. Pradhan, D. E. Herrick, J. W. Tierney and I. Wender, *Energy & Fuels*, **5** 712 (1991).
6. V. R. Pradhan et al., *Energy & Fuels*, **5** 497 (1991).
7. K. J. Huttinger and R. Minges, *Fuel*, **64** 364 (1985).
8. R. E. Marganski and R. L. Rowell, *J. Disp. Sci. Tech.*, **4**(4) 415 (1983).
9. A. D. Stuart, *Fuel*, **65** 1003 (1986).
10. G. M. K. Abotsi and K. Osseo-Asare, *Int. J. Min. Proc.*, **21** 225 (1987).