Surface Modified Coals for Enhanced Catalyst Dispersion and Liquefaction

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SURFACE MODIFIED COALS FOR ENHANCED CATALYST DISPERSION AND LIQUEFACTION

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The aim of this study is to enhance catalyst loading and dispersion in coal for improved liquefaction by preadsorption of surfactants and catalysts on the coal. During this reporting period, the effects of dodecyl dimethyl ethyl ammonium bromide (DDAB) (a cationic surfactant), sodium dodecyl sulfate (SDS) (an anionic surfactant), Triton X-100 (a neutral surfactant), and ferrous sulfate (as a catalyst precursor) on the coal surface charge at various pH values were determined.

The results of the zeta potential measurements suggest that ferrous sulfate as catalyst precursor creates a distinctly different condition on the coal surface compared to that of molybdenum as reported in the previous progress reports. The effects of the adsorption of the surfactants also varied distinctly with the type of surfactant. With the adsorption of DDAB, the cationic surfactant, the surface charge was more positive. The opposite effect was observed for the SDS, the anionic surfactant. The coals treated with Triton X-100, the neutral surfactant, also showed an overall negative surface charge density. The adsorption of the catalyst precursor (ferrous sulfate) resulted in a net negative charge on the coal surface. Additional studies are in progress to confirm and explain the observed results.
INTRODUCTION

Coal surface contains both hydrophobic and hydrophilic sites. However, little work has been done to understand the effects of this dual character of the coal surface on catalyst loading and dispersion for coal conversion. When added from organic solution, the catalyst will be attracted to the organic sites on the coal but it will be repelled by the hydrophilic sites. This will produce low liquefaction activity. By adsorbing appropriate surfactants onto coal, the hydrophilic heads of the surfactants will be adsorbed onto the oppositely charged sites on the coal while the organic portions will be oriented towards the organic solution. This should promote hydrophobic interaction between the hydrophobic catalyst solution and the catalyst precursor. The organic portion of the surfactant can also be adsorbed onto the hydrophobic site of the coal, with the hydrophilic head oriented towards the aqueous solution. This should enhance the uptake and dispersion of water-soluble catalyst precursors.

The high liquefaction activities of molybdenum compounds are well known (1,2). However a major challenge which is facing the application of this catalyst on a commercial scale is the inability to achieve high levels of catalyst dispersion on coal. The need for high catalyst dispersion is especially important because of the high cost of molybdenum. Hence, improved techniques for molybdenum dispersion in coal are needed for the enhancement of coal liquefaction activity. To reduce catalyst cost, mixtures of
iron and molybdenum have been proposed. However, the activity of iron is much less than that of molybdenum. The availability and low cost of iron can be a major economic incentive for coal liquefaction on commercial scale. The aim of this work is to enhance the liquefaction activities of coal by improving dispersion of molybdenum and iron in coal by pretreatment with surfactants.

**EXPERIMENTAL**

The Illinois No.6 coal (DECS-24) used in this experiment was supplied by the Penn State Coal Sample Bank. The characteristics of the coal including proximate analysis and elemental analysis have been provided in previous reports (3,4).

The first phase of this investigation involved the preparation of the eight samples to be tested by electrokinetic measurements. These samples were prepared by adding 5.0 grams of 60 mesh (U.S. standard sieve) particles of coal to 25 ml of aqueous solutions of 0.1 M DDAB, SDS, or Triton. The samples were shaken for 24 hours using a Burrel Wrist Action Shaker. Thereafter, the slurries were filtered using gravity filtration, and air-dried. Next, the dried coals were loaded with 25 ml of 1000 ppm ferrous sulfate solution, which served as the catalyst precursor. Finally, the samples were again allowed to shake for 24 hours, followed by filtration and drying.

Each of the eight samples endured a final preparation for electrokinetic measurements by undergoing ionic strength adjustments.
Slurries were prepared by placing 2.5 grams of each sample in 500 ml of deionized water. The ionic strength adjustment was made by adding 0.04 grams of sodium nitrate to this solution. After thorough adjustment by mechanical agitation for 20 minutes the heavier particles were allowed to settle, while the suspended ones were decanted and transferred to a one liter volumetric flask. The suspensions were divided into 5 flasks, each containing 50 ml portions. After recording the original pH values, pH adjustments were made using 1M HCl or 0.5M NaOH solutions to achieve the desired values. The samples were shaken on a mechanical agitator for 4 hours, followed by redetermination of the equilibrium pH values. The zeta potentials were subsequently measured at room temperature using a Pen Kem Model 501 zeta meter.

RESULTS AND DISCUSSION

The results for the zeta potential measurements are shown in Figures 1-5 for the parent coal and coal samples treated with various types of surfactants and loaded with the catalyst precursor. The behavior of the coals illustrated by these figures is quite different from the coals previously studied (3). These preliminary results suggest that the catalyst precursor ferrous sulfate (FeSO₄·7 H₂O), creates distinctly different conditions on the coal surface as opposed to that of molybdenum (3).

As shown in Figure 1, the effects of the adsorption of the surfactants varies distinctly. It is apparent that the surface chemistry on the surface of
the coal plays a major role. Over a wide range of pH values the surface charge densities are dependent upon surface oxygen functionality. With the adsorption of DDAB, the cationic surfactant, the surface charge becomes more positive. However, we see the opposite effect occurring with the adsorption of SDS, the anionic surfactant. The zeta potential values of the coal treated with Triton X-100, the neutral surfactant, also indicate an overall negative surface charge density. These results show that the surface charge of the coal samples varies as a function of the surfactant type.

The zeta potential results of the parent coal treated with SDS and the catalyst, ferrous sulfate, are shown in Figure 2. Between pH 5 and pH 8, there is a large density of negative surface charge. This may be attributed to the fact that the dissociation of the carboxylic group is enhanced in the presence of OH\(^{-}\). This causes a net negative charge on the surface of the coals.

The organic portions of the SDS anion (RSO\(_3^-\) Na\(^+\)) may be repelled by the ionic sites on the surface, and attracted to hydrophobic sites. On the contrary, the hydrophilic portion of the SDS molecule has an electrostatic attraction to the ionic sites on the coal surface. This in turn, causes an enhancement of the surfactant on the coal surface, thereby leading to a net negative surface charge. These conditions are optimum for the loading of the Fe\(^{2+}\) catalyst. It may be noted that the addition of the catalyst alone causes the surface charge of the coal to become more negative. The reasons for this
occurrence are still being investigated. However, it is evident that when using the surfactant-catalyst combination the catalyst does reduce the overall negative surface charge.

The zeta potential of the coals treated with the cationic surfactant DDAB $(R^+Br^-)$ and the catalyst are depicted in Figure 3. This figure shows a graphic representation much different from that of the anionic surfactant, SDS. Altogether, a net positive surface charge trend occurred. This effect is probably due to a greater amount of surfactant-coal interaction, and the potential for less catalyst loading as a result of repulsion between the catalyst $(Fe^{2+})$ and the positive charge on the coal surface. Due to the fact that the surface has a net positive charge, there should be very little catalyst adsorption due to electrostatic interactions.

The trends occurring in Figure 4 show very little difference in the adsorption of catalyst versus that of the surfactant, or the combination of the two. Triton X-100 is a neutral surfactant. It is obvious that it has very little, if any, effect on the surface of the enhancement of the adsorption of the catalyst.

The final figure, Figure 5, depicts a comparison of all the surfactant-catalyst interactions. It is a graphical summary of the effects of each surfactant upon the dispersion of catalyst loading.
Further studies are needed to more accurately assess the effects of surfactants and catalyst precursors. However, it is clear from the preliminary results shown here that surfactants and catalyst precursors have a significant influence on the coal surface charge. Future studies will reveal new information regarding the usefulness of this technique for maximum catalyst dispersion. The results attained in this study will be confirmed by establishment of error bars in the data. In addition to this, liquefaction testing for molybdenum samples will also be completed. A comparison of dispersion and liquefaction activities of iron, molybdenum and/or combinations of these metals will help us to determine the validity of the proposed technique for enhanced catalyst dispersion.

REFERENCES

Figure 1. Zeta potential of parent coal treated with iron and each surfactant.
Figure 2. Zeta potential measurements of the parent coal treated with SDS and iron.
Figure 3. Zeta potential measurements of the parent coal treated with DDAB and iron.
Figure 4. Zeta potential measurements of the parent coal treated with Triton X-100 and iron.
Figure 5. Zeta potential measurements of each surfactant and iron.