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SURFACE MODIFIED COALS FOR ENHANCED CATALYST DISPERSION AND LIQUEFACTION DISCLAIMER

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ABSTRACT

The aim of this work is to enhance catalyst loading and dispersion in coal for improved liquefaction by preadsorption of surfactants onto coal. The application of surfactants to coal beneficiation and coal-water slurry preparation is well known. However, the effects of surfactants on catalyst loading and dispersion prior to coal conversion processes have not been investigated. The current work is focused on the influence of the cationic surfactant dodecyl dimethyl ethyl ammonium bromide (DDAB) and sodium dodecyl sulfate (SDS, anionic) on the surface properties of a bituminous coal and its molybdenum and iron uptake from solution. In the previous report, it was shown that molybdenum loading onto the coal was enhanced by preadsorption of DDAB. The optimum concentration of this surfactant for effective adsorption of molybdenum at the natural pH of the coal slurry has been determined to be in the 0.1 to 0.25 M range. Preadsorption of SDS onto the coal was found to increase the uptake of iron by the coal; iron loading increased with increase in the concentration of the catalyst precursor. This observation is attributed to the increase in the negative surface charge properties of the coal with increase in the concentration of the surfactant. The results of the study show that DDAB enhances the adsorption of molybdenum whereas SDS is more effective for iron loading onto Illinois No. 6 (DECS-24) coal.

INTRODUCTION

The goal of this work is to modify coal surface properties by adsorbing surfactants and thereby improve catalyst adsorption and dispersion, and enhance coal liquefaction activities. Coal surface contains both hydrophobic and hydrophilic sites. However, this dual character of coal surface is generally not taken into consideration when loading coal with catalysts from organic and aqueous solutions. When added from organic solutions, the catalyst will be attracted to the organic sites on the coal but it will be repelled by the hydrophilic sites. This will produce an uneven distribution of the catalyst on the coal, result in poor catalyst dispersion, and 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 will 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 (1-3). The catalyst may be sulfided in-situ or converted into the sulfide form by the sulfur in the coal. Previous reports showed that improved techniques for molybdenum dispersion in coal are needed to

improve its liquefaction activity. In addition, it is well known that mixtures of iron and molybdenum catalysts are effective for coal liquefaction. The availability and low cost of iron can be a major economic incentive for coal liquefaction on a commercial scale. The aims of this work are to enhance the liquefaction activities of coal by improving the dispersion of molybdenum and iron in coal via pretreatment with surfactants.

EXPERIMENTAL

The Illinois No.6 coal (DECS-24) used in this study 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 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 adding 2.0g of coal to 25 mL of 0.005M aqueous solution of iron and 25 mL of various concentrations of SDS. The SDS concentration ranged from 0.5×10^{-4} to 0.5×10^{-2} M. A set of six samples were prepared for each surfactant concentration. The average natural, unadjusted pH of the slurries was 4.2. Iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used as the source of iron. Two sets of the coal-water slurries, one set without surfactants and the other without coal, were used as controls. The samples were shaken on a mechanical shaker for 24 h. The samples were then filtered and the filtrates were analyzed for iron by Galbraith Laboratories, Knoxville, TN. In another set of experiments, the influence of various concentrations of DDAB or SDS on molybdenum

loading was investigated. Ammonium molybdate (VI) tetrahydrate (AMT) was used as the molybdenum source.

The effects of DDAB on the zeta potentials of the coal have been reported previously. In this report, the influence of SDS on the surface chemistry of the coal was measured using 5.0 g of coal per liter suspended in deionized water. The measurements were conducted on 25mL samples to which 25mL of 0.2M, 0.02M, or 0.002M SDS solution had been added. The pHs of the samples were measured and then adjusted with acid (HCl) or base (NaOH) solution. The samples were equilibrated for 4 hours by mechanical agitation using a Burrel Wrist Action Shaker and the equilibrium pH of each sample was recorded. The zeta potential of each sample was measured at room temperature using a Pen Kem Model 501 zeta meter. Details of the procedure have been provided previously (4-6).

RESULTS AND DISCUSSION

The zeta potential results in Figure 1 show that the coal is negatively charged within the pH range investigated and that the charge density increased with increase in the slurry pH. This behavior is attributed to enhanced dissociation of the surface carboxylic acid group as the slurry pH was increased (4,5). Addition of SDS to the coal slurry increased the negative zeta potentials compared to that of the parent coal. The surface charge densities increased with increase in the concentration of the surfactant, indicating that the extent of surfactant loading increased as its concentration was raised. In

aqueous solution, SDS ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$) will dissociate to produce the dodecyl sulfonate anion ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$). In contrast to the effect of DDAB reported earlier, the zeta potentials of the coal particles became more negative than those of the parent coal in the presence of SDS, as shown in Figure 1. The negative charge density increased with increase in pH and in the concentration of SDS. Since the surface of the raw coal is negative, the adsorption of SDS must occur through the hydrocarbon chain of the molecule, with the anionic head oriented towards the aqueous solution.

The apparent low concentration of DDAB required for effective molybdenum loading onto this coal is important since this will reduce the cost of surfactant required for efficient catalyst dispersion and liquefaction and make the process economically attractive. The observed molybdenum adsorption pattern can be explained by the electronic charges on the coal surface and on the molybdenum species. In aqueous solution, AMT will dissociate to form various molybdenum oxyanions which are pH dependent (7). It is reported that $\text{Mo}_8\text{O}_{26}^{4-}$ predominates below pH 2 whereas $\text{Mo}_7\text{O}_{24}^{6-}$ exists as the dominant species between pH 2 and 6. MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ occur in the pH 6 to 8 range; MoO_4^{2-} predominates above pH 8. Thus, the adsorption of the molybdenum species should be promoted by the positively charged DDAB sites on the coal. As discussed in the previous report, the zeta potentials of the coal became more positive as the concentration of DDAB increased. Thus, the increase in molybdenum loading can be explained by the enhanced positive charge on the coal surface following the adsorption of the surfactant (DDAB).

Figure 2 also shows that in contrast to DDAB, SDS had very little effect on the uptake of Mo at the SDS concentrations investigated. This could be due to coulombic repulsion between the adsorbed anionic surfactant and the molybdate ions. The mechanism of molybdenum adsorption in the presence of SDS is currently unknown and it is the subject of further studies.

The uptake of iron by the SDS-treated coal is shown in Figure 3. It can be observed that similar iron loadings occurred on the coal at low SDS concentrations (5×10^{-4} and 5×10^{-5} M) and in the absence of the surfactant. However, a significant increase in iron uptake occurred when the SDS concentration was raised to 5×10^{-3} M. As discussed earlier in this report, the surface of the coal particles became more negative with increase in the quantity of SDS added to the slurry. Hence, the increased iron loading is ascribed to coulombic attraction between the positively charged metal ions (Fe^{2+}) and the anionic coal surface.

In summary, it has been shown that the uptake of molybdenum is promoted by preadsorption of dodecyl dimethyl ammonium bromide (DDAB) onto the surface of Illinois No. 6 coal, DECS-24. The low concentration of this surfactant required to attain a constant level of molybdenum loading suggests that economic benefits can be realized if high catalyst dispersion can be obtained by the use of small quantities of the surfactant. Addition of SDS to the coal enhanced the uptake of iron, compared to that on the parent coal, through the creation of negative sites on the coal surface as supported by zeta potential data.

The effects of the surfactant-enhanced loading of the catalysts on coal liquefaction activities are currently under investigation.

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Figure 1. Effect of sodium dodecyl sulfate (SDS) on the zeta potentials of Illinois No. 6 (DECS-24) coal at various pHs.

Figure 2. Effect of Surfactant Concentration on Molybdenum Adsorption by DECS-24 Coal at Natural pHs ($4.57 \geq \text{pH} \leq 5.33$)

Figure 3. Iron Adsorption as Function of Shaking Time and SDS Concentration