

CATALYTIC LIQUEFACTION OF SURFACTANT-TREATED COALS

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INTRODUCTION

The purpose of this study is to critically study the efficiency of the adsorption of catalysts onto coals that have been treated with surfactants. The diminishing supplies of petroleum requires that research be conducted to produce coal-derived liquids as supplements for transportation fuels. Catalyst dispersion on coal is dependent upon the nature of the catalyst and the coal surface. Pre-treatment of coal surface with an appropriate surfactant can enhance catalyst dispersion.¹ The aim of this work is to achieve improved catalyst dispersion on coal by preadsorption of various cationic, anionic, and neutral surfactants such as dodecyl dimethyl ethyl ammonium bromide (DDAB), sodium dodecyl sulfate (SDS) and Triton X-100 onto coal.

Potentially, this ongoing research can result in the development of a low cost technique for efficient dispersion of iron and molybdenum catalysts in coal by preadsorption of surfactants onto coal. This should make the coal surface hydrophobic and enhance the adsorption and dispersion of iron/molybdenum-containing organic compounds and carbonyls, and thus provide information about the roles of coal hydrophilic and hydrophobic sites on the chemistry of adsorption of coal conversion catalysts. Appropriate selection of the surfactants used for coal-water slurry preparation should allow successful integration of this catalyst loading technique into the coal-water slurry mode of transport which will allow sufficient time for catalyst penetration and dispersion in the coal.

EXPERIMENTAL

An Illinois No. 6 coal (DECS-24), obtained from the Penn State Coal Sample Bank, was used in this work. 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. Elemental analysis gave 11.6% ash, 57.3% carbon, 4.0% hydrogen, 1.0% nitrogen, 4.8% sulfur, and 8.1% wt oxygen (by difference). The surfactants were supplied by Aldrich Chemical Co. Ammonium molybdate(VI) tetrahydrate (AMT) was used as the molybdenum catalyst precursor.

The zeta potentials of the raw coal and its samples that were treated with the surfactants were measured at room temperature using a Pen Kem 501 zeta meter as described previously.² Zeta potential measurements allowed the determination of the surface charge properties of the coals. The effect of surfactants and pH on molybdenum adsorption was determined by elemental analysis for molybdenum after the adsorption studies using atomic absorption spectrophotometry. Pretreatment of the coal-water slurry with surfactants and subsequent catalyst loading was done by ion-exchange technique using a Burrell Wrist Action Mechanical Shaker, Model 75, manufactured by Burrell Corporation, Pittsburgh, PA.

Following the surfactant and catalyst loadings, the surfaces of the coal samples were examined using Atomic Force Microscopy (AFM) at the Savannah River Ecology Laboratory (SREL), Aiken, SC. The instrument used was a Burleigh ARIS-3300 AFM with two sample scanning modes. AFM is a variation of the Scanning Tunneling Microscope and it measures the interatomic forces and surface features.^{3,4} The samples were mounted on epoxy and imaged by tapping with the probe tip of the AFM imaging instrument. Tapping mode imaging overcomes the limitation of conventional scanning modes

(contact and non-contact mode), by alternately placing the tip of the scanning probe in contact with the surface to provide high resolution and then lifting the probe tip off the surface to avoid dragging the tip across the surface. The technique allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely held to their substrate, or otherwise difficult to image by other AFM techniques.

The effectiveness of the catalyst loading technique was measured by liquefaction activities of the raw coal and the catalyst-loaded samples. Liquefaction studies were conducted in a stainless steel batch microautoclave reactor. The internal volume of the reactor including all tubing and connections was 60 mL. For continuous monitoring of pressure and temperature during the experiment, an internal thermocouple and pressure transducer were used. The samples were tested using 6.6g of solvent, 3.3 g of coal and 6.9 MPa (1000 psi) ambient hydrogen pressure. The reactor was then attached to the rocker arm of a motor that vibrated at 180 cycles/min, and plunged into a pre-heated sandbath that was heated to 425°C in 40 minutes. This temperature was maintained for 30 minutes, after which the reactor was removed and cooled with water. The liquid and solid products were removed from the reactor using tetrahydrofuran (THF). Coal conversions were calculated based on THF and heptane solubility.

RESULTS AND DISCUSSION

Measurements of the surface charge densities of the coal samples gave the results expected for the surfactants. The raw sample produced negative zeta potentials over the pH range investigated. As discussed elsewhere,² the coal particles showed positive zeta potentials as a result of the adsorption of DDAB. Since DDAB is cationic, the positive charge density on the coal can be explained by the coulombic attraction of the surfactant to the negatively charged sites on the coal. The opposite effect was observed for the anionic surfactant, SDS.

As shown in Figure 1, the maximum zeta potential of the raw coal was about -80 mV. However, adsorption of 0.25 and 0.1 M Triton reduced the negative charge density appreciably. This is surprising since Triton is a neutral surfactant. Reasons for this behavior will be sought through further studies. The effects of surfactant concentration in the adsorption of molybdenum is shown in Figure 2. As shown this figure, a higher molybdenum adsorption occurred when DDAB was used. The minimum amount of this surfactant required to saturate the surface is about 0.1 mol/L. However, the opposite effect (low catalyst loading) was observed when the anionic surfactant (SDS) was used. There is very little adsorption of molybdenum, which is ascribed to the fact that SDS and the molybdenum oxyanions in solution are negatively charged and create repulsive forces.

The results for the Atomic Force Microscopy studies are apparently consistent with the results observed from zeta potential and catalyst loading experiments. Figure 3 is a scan of the surface of the untreated coal, which shows that the surface has rough, uneven appearance with several crevices. The surface of the coal treated with SDS is depicted in Figure 4. In this micrograph rod-like structures are distributed in layered patterns on top of the rough surface of the coal. These rods are attributed to adsorbed surfactants and/or surfactant-molybdenum complexes onto the coal surface. Figure 5 shows the coal surface which has been treated with DDAB followed by molybdenum loading. This image shows a smoother, more defined coal surface, with pellets randomly distributed on the surface. However, the composition of the pellets is unknown at this time. The surfaces of the samples were imaged in the dimension range from 5 μ m to 100 nm. The imaging of the samples posed some difficulties in the area of uneven topology. Imaging even small areas of the particle surface was difficult since the topology was typically greater than the length of the AFM probe tip. In order to obtain better images so that definitive comparisons between samples can be made, further AFM studies will be conducted with thin polished sections of the samples. Another alternative would be to fractionate the samples and image very small (< 500 nm) size particles.

The liquefaction data are presented in Table 1. As can be seen from the results, the conversions for the raw coal and its sample that was treated with the surfactant (Triton X-100) were 72 and 78 wt%, respectively. However, a higher level of conversion (96 wt. %) was observed for the surfactant-assisted molybdenum impregnated coal. This result is also higher than that obtained for the nonsurfactant assisted molybdenum loading (89 wt %) and suggest that the surfactant may have enhanced the dispersion of the molybdenum catalyst. Further testing is in progress to evaluate the effects of other surfactants on the activities of the catalysts.

This work has shown that molybdenum loading can be enhanced by treatment of an Illinois No. 6 coal with cationic surfactants, such as DDAB prior to catalyst addition from solution. Compared to the untreated coal, higher liquefaction activity was obtained when the coal was pretreated with Triton X-100.

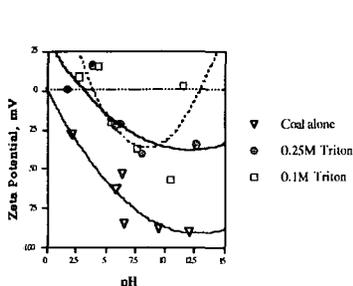


FIGURE 1. Zeta Potential of the Raw and the Triton-treated coals.

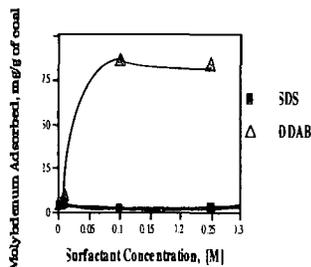


FIGURE 2. Dependence of molybdenum loading on DDAB and SDS concentration.

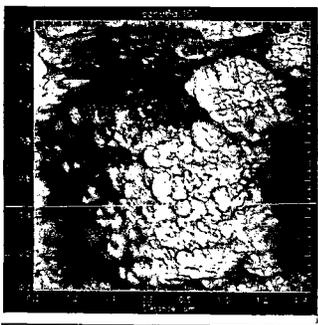


FIGURE 3. Atomic Force Micrograph of the raw coal.



FIGURE 4. Atomic Force Micrograph of the coal surface after treatment with SDS

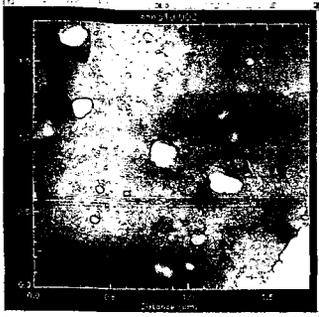


FIGURE 5. Atomic Force Micrograph of the DDAB-treated coal.

Sample	THF Solubles (Total Coal Conversion to Liquids)	Hexane Solubles (Oils)
Coal + Mo + Triton	96.2%	46.7%
Coal (Original)	72.4%	33.8%
Coal + Triton	77.9%	33.2%
Coal + Mo	90.0%	50.0%

TABLE 1. THF and Hexane conversions of the various coal samples

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