

The Effect of Promoter Metal Concentration on the Catalytic Activity of Sulfated Hematite for the Liquefaction of a Subbituminous Coal

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Abstract

The application of dispersed iron-based catalysts to the liquefaction of low rank coals has been well documented since the 1930's. More recent research has attempted to improve their activity, primarily by reduction in the particle size or by modification through the introduction of various promoters. The use of sulfated hematite has been shown to yield positive results for the liquefaction of a subbituminous coal. The addition of promoter metals such as molybdenum and tungsten were shown to effect further improvements in activity. This study has shown that the addition of promoters in combination, such as nickel with molybdenum, may significantly increase activity at low promoter concentrations and, potentially, low cost. The effects of the promoter metals nickel, cobalt, tungsten, and molybdenum, individually and in combination will be presented. Molybdenum showed the highest increase in activity for the single promoter metals examined. While the activity of tungsten and cobalt, when used in combination with molybdenum, appeared to be essentially additive, the combination of nickel and molybdenum exhibited a synergistic effect, resulting in high conversions at low promoter loading.

Introduction

Iron-based catalyst precursors have long been known to improve the conversion of low rank coals. Efforts to improve the activity of these catalyst has centered primarily on attaining very small particle size, improved dispersion, and chemical modification of the catalyst. The use of oil-soluble precursors, such as iron carbonyl, have demonstrated significant catalytic activity, presumably through their being efficiently dispersed in the coal-solvent slurry. However, one study found that an oil-soluble precursor could lead to the formation of large crystallites more rapidly than a small particulate precursor.¹ The loss of dispersion is expected to be associated with a reduction in catalyst activity.

Small particle iron oxides have been shown to have moderate activity for coal liquefaction. The addition of sulfate groups to hematite (Fe_2O_3) has been shown to further improve the activity of these catalysts.^{2, 3, 4, 5, 6} Sulfated hematites have been produced by two methods. The first involves the addition of a source of sulfate ion to a previously formed goethite (FeOOH) particle by washing with sulfuric acid.⁵ The second method involves the precipitation of goethite in the presence of a source of sulfate ions.⁷ The particles may then be calcined to form $\text{Fe}_2\text{O}_3/\text{SO}_4$. The nomenclature used does not denote a stoichiometric relationship between the iron and sulfate group but rather indicates SO_3 chemisorbed on the surface of the iron oxide. Both methods of preparation have been shown to yield improved activity for iron oxide catalyst precursors.

The high catalytic activity of molybdenum is well established. However, the use of a dispersed molybdenum catalyst in a coal dissolution process is cost prohibitive, except in very low concentrations, due to difficulties associated with catalyst recovery. Pradhan and coworkers found that the addition of up to 5 wt% molybdenum or tungsten based on iron as a promoter to sulfated hematite resulted in a significant increase in activity.⁸ As with most iron-based catalysts the addition of a source of sulfur is critical to achieving the maximum activity. The promoted sulfated hematites demonstrated significant activity at low catalyst loadings (<0.4 wt% iron on coal).

The purpose of the current study was to determine the effect of promoter metals on the

activity of sulfated hematite when used singly and in various combinations. Molybdenum, tungsten, nickel, and cobalt were utilized based on their catalytic activities in other systems.

Catalyst Synthesis

The iron based catalysts used in this study were prepared using an aqueous precipitation technique. This method involves the coprecipitation of iron and a promoter metal in the presence of sulfate ions. Urea was used to effect the precipitation of ferric ammonium sulfate (iron alum), following the method of Kotanigawa et al.⁷ Molybdenum was incorporated by addition of ammonium molybdate to the iron alum solution, as described previously.⁹ Ammonium nickel sulfate hydrate and cobalt sulfate hydrate were used to add nickel and cobalt, respectively. The precipitated catalysts were filtered and dried in an air flow oven overnight, and then calcined in air at 475 °C for 30 minutes.

The promoted sulfated hematite catalysts were analyzed by XRD, XPS, TEM, SEM, and nitrogen BET adsorption. The results of electron microscopy have shown that the catalysts consist of loose agglomerations of particles with an acicular shape and average dimensions of ~10x50 nm. Surface areas were measured by nitrogen BET adsorption and were found to be in the range 100-200 m²/g. The addition of up to 10 wt% of molybdenum had little effect on the particle size and no apparent effect on the major phase identified by XRD, to be α -FeOOH with trace α -Fe also present in the as formed precipitate. After calcination, the major phase was α -Fe₂O₃ with some α -Fe still present. The relative amount of α -Fe does not appear to be affected by calcination.

Elemental analysis of the sulfated hematites indicated that the sulfur content was between 2-6 wt%. It has been reported that the sulfur is present on the surface of the hematite as chemisorbed SO₃. Analysis by XPS supported this supposition, showing that the surface sulfur concentration was significantly higher than in the bulk. It was also found that the sulfur content decreased with increasing molybdenum concentration. This may indicate that molybdenum is chemisorbed as MoO₃ displacing the sulfur on the surface. The XPS studies further show that the surface concentrations of molybdenum, sulfur, and tungsten are substantially higher than the bulk concentrations. Nickel and cobalt, on the other hand, have similar bulk and surface concentrations indicating that they may be substituted into the iron oxide matrix. Table 1 shows a comparison of bulk and surface concentrations for a nickel-molybdenum promoted sulfated hematite, clearly demonstrating this result. It follows from Goldschmidt's rules of substitution that the hexavalent ions, Mo, W, and S cannot substitute for iron while the nickel and cobalt can.¹⁰

Experimental

The catalytic activity of the particles for the liquefaction of Black Thunder subbituminous coal in tetralin was determined using 50 ml horizontal microautoclave reactors. In these experiments, the reactors were loaded with 3 g of as-received coal, 5 g tetralin and 0.07g dimethyldisulfide (DMDS) added as a sulfiding agent. The catalyst was added at an iron loading of 1 wt% with respect to maf coal. The reactors were sealed and pressurized to 1000 psig (cold) with hydrogen, then agitated in a heated fluidized sand bath at 400 cycles/minute. The reactions were carried out at 415°C for 60 minutes, after which the reactors were quenched in a cool sand bath. The use of this system allowed rapid heating and cooling of the reactor thereby reducing errors associated with prolonged heating times.

The total conversion was defined by THF solubility while the THF soluble-pentane insoluble product was defined as preasphaltenes + asphaltenes (PA&A). The THF insoluble product was defined as IOM and the pentane soluble fraction as oils. The total conversion as well as PA&A yield were determined directly and the oil yield was determined by difference. The gas yield was determined directly by gas chromatography. All conversions are reported on a maf coal basis.

Results

The use of the sulfated hematite resulted in an increase in total conversion to 88.1% from 84.8% for the blank thermal baseline conversion. The increase in conversion was due entirely

to an increase in PA&A yield from 42.0% to 46.4% with no substantial change in oil or gas yield. Under the conditions used in this study, the gas yields were unaffected by any of the catalysts. These results were comparable to those obtained using a super fine iron oxide (SFIO) catalyst at similar iron loadings. The SFIO catalyst is of smaller diameter (3 vs 19 nm) and has a higher surface area (190 vs 100 m²/g) than to the sulfated hematite.

Figure 1 shows the effect of molybdenum concentration on the conversion of the Black Thunder coal in tetralin. The addition of 1 wt % molybdenum as a promoter metal to the sulfated hematite resulted in no significant increase in total conversion. However there was a slight increase in selectivity increasing the oil yield from 34.4% to 38.6%. The molybdenum concentration of 1 wt% with respect to iron corresponds to a loading of 100 ppm molybdenum on an maf coal basis. At this low loading the effect of molybdenum is very modest.

Increasing the promoter concentration to 5 wt% molybdenum on iron resulted in an increase in total conversion to 92% compared to 88% for the unpromoted sulfated hematite. Further, an increase in oil yield and a decrease in PA&A yield was also observed. This represents a significant improvement in the activity and selectivity of the sulfated hematite at a molybdenum loading of only 500 ppm on maf coal.

Increasing the promoter concentration to 10 wt% molybdenum on iron resulted in a further increase in both conversion and selectivity. The increase in total conversion arises from an additional increase in oil yield and a decrease in PA&A yield. The net effect of the addition of 1000 ppm molybdenum on maf coal loading is to increase total conversion by 6% and oil yield by 14% compared to the unpromoted sulfated hematite.

The addition of 1.4 wt % nickel resulted in a slight increase in total conversion over the unpromoted case, unlike the other singly promoted catalysts. This increase was due entirely to an increase in PA&A yield, as the oil yield remained unchanged (within experimental error). In contrast, the other metals produced substantial increases in oil yield. The addition of 2.5 wt % cobalt caused a negligible increase in total conversion but a slight increase in oil yield. The effect of 4 wt % tungsten yielded the same results as the 2.5 wt % cobalt, within experimental error. Therefore, of these three metals, it is found that 500 ppm tungsten and 250 ppm cobalt (maf coal) have very similar catalytic activity for coal liquefaction, while 140 ppm nickel (maf coal) had slightly higher activity for total conversion but lower selectivity to oils.

Of the singly promoted hematites, molybdenum displays the highest activity for conversion and also the greatest selectivity to oils. Further, both the activity and selectivity of the catalyst increase with increasing molybdenum concentration. However, due to the significant cost associated with molybdenum, a loading of 1000 ppm on maf coal would be prohibitively expensive. Therefore the use of other promoters in combination with molybdenum was explored.

Cobalt /molybdenum doubly promoted sulfated hematite demonstrated considerable catalytic activity. As shown in Figure 2 the addition of 1 wt % molybdenum and 0.5 wt % cobalt (based on iron) to the sulfated hematite increased the total conversion to a level close to that obtained with 5 wt% molybdenum, and greater than that obtained with 2.5 wt % cobalt alone. This may indicate a possible synergistic effect between the molybdenum and the cobalt promoters. The oil yield was increased to 40 %, only slightly higher than the oil yield obtained with 1 wt % Mo. Thus, at a promoter concentration of 100 ppm molybdenum and 50 ppm cobalt (maf coal), the activity of the catalyst for total conversion approaches that of 500 ppm molybdenum, with slightly lower selectivity to oils.

Similar results were obtained for hematite doubly promoted by molybdenum and tungsten. The addition of 1 wt% molybdenum and 0.8 wt % tungsten gave a total conversion of 92 % and an oil yield of 40%. In Figure 3, the molybdenum/tungsten promoted catalyst is compared to singly promoted molybdenum (5wt%) and tungsten (4wt%) catalyst. In combination with molybdenum, cobalt and tungsten appear to have similar effects.

A combination of nickel and molybdenum yielded somewhat better results. The use of 0.9 wt

% molybdenum and 0.7 wt% nickel as promoters produced marginally higher total conversion than the cobalt/molybdenum and tungsten/molybdenum promoters. More importantly, however, is the fact that very high oil yields were obtained. As shown in Figure 4, the oil yield exceeds that obtained with 5 wt% molybdenum and strongly suggests a synergistic effect between the nickel and molybdenum. The combination of 90 ppm molybdenum, 70 ppm nickel, with 1 wt% iron on maf coal gave the highest selectivity to oils of the doubly promoted catalysts tested.

The promising results of these studies have prompted further interest in these catalysts. By varying the concentration of promoter metals it may be possible to obtain higher conversions or, more probably, to increase the selectivity to oils. Studies are currently underway to optimize the promoter metal concentrations to maximize catalytic activity and selectivity.

References

1. Djega-Mariadassou, G., *et al. Fuel Processing Technology* 12, 143-153 (1986).
2. Hattori, H., Yamaguchi, T. & Tanabe, K. *Fuel Processing Technology* 8, 117-122 (1984).
3. Tanabe, K., *et al. Fuel Processing Technology* 14, 247-260 (1986).
4. Yokoyama, S., Yamamoto, M., Yoshida, R., Maekawa, Y. & Kotanigawa, T. *Fuel* 70, 163-168 (1991).
5. Pradhan, V.R., Tierney, J.W., Wender, I. & Huffman, G.P. *Energy & Fuels* 5, 497-507 (1991).
6. Pradhan, V., Tierney, J.W. & Wender, I. *ACS Preprint - Fuel* 35, 793-800 (1990).
7. Kotanigawa, T., Yokoyama, S., Yamamoto, M. & Maekawa, Y. *Fuel* 68, 618-621 (1989).
8. Pradhan, V.R., Hu, J., Tierney, J.W. & Wender, I. *Energy & Fuels* 7, 446-454 (1993).
9. Hager, G.T., Givens, E.N. & Derbyshire, F.J. *ACS-Division of Fuel Chemistry Preprints* 38, 1087-1092 (1993).
10. Faure, G. *Principles and Applications of Inorganic Geochemistry* 1-626 (Macmillan Publishing Company, New York, 1991).

Table 1. Elemental Composition of Promoted Sulfated Hematite.

Element	Bulk wt %	Surface wt %
Molybdenum	4.0	7.5
Nickel	2.3	2.5
Sulfur	2.7	4.7

Figure 1. Effect of Molybdenum Loading on Conversion

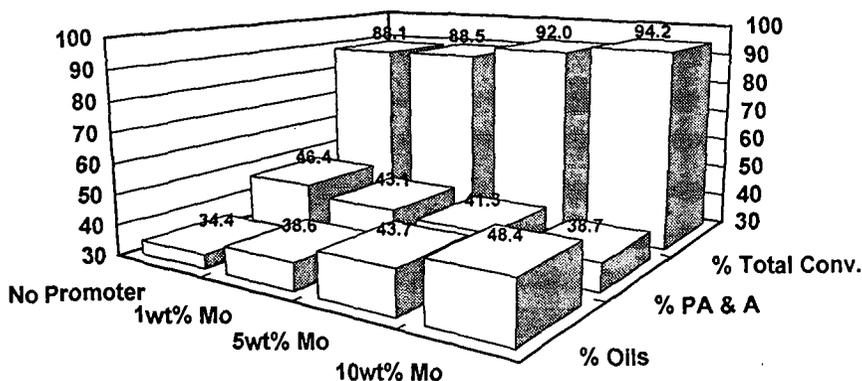


Figure 2. Effect of Molybdenum and Cobalt on the Activity of Sulfated Hematite

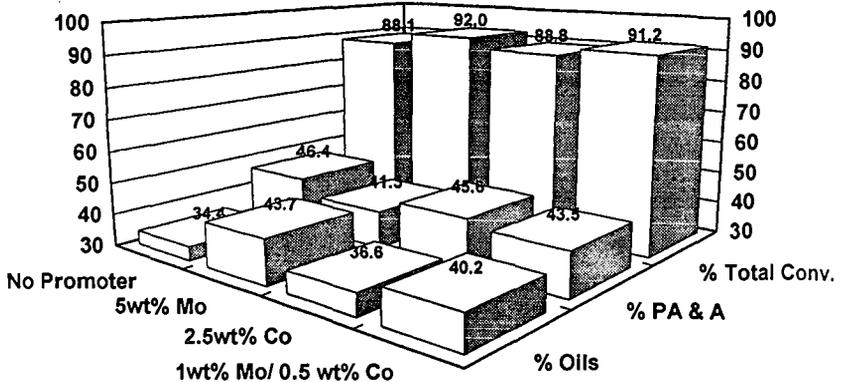


Figure 3. Effect of Molybdenum and Tungsten on the Activity of Sulfated Hematite

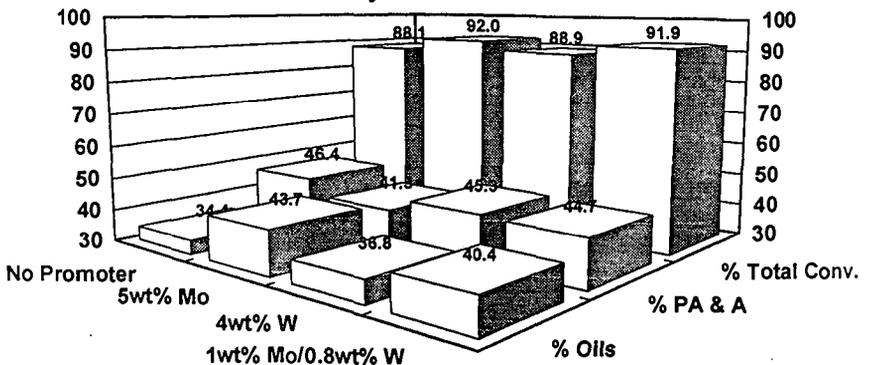


Figure 4. Effect of Molybdenum and Nickel on the Activity of Sulfated Hematite

