The Effect of Promoter Metals on the Catalytic Activity of Sulfated Hematite for Model Compound Reactions

G. T. Hager, R. Ochoa, E. N. Givens, P. C. Eklund, F. J. Derbyshire
Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511-8433

Abstract

Iron based catalysts have long been known to enhance the conversion in a direct coal liquefaction process. Attempts to increase the moderate activity of these catalysts have focussed on reducing particle size, enhancing and maintaining dispersion, and modifying the structure by addition of promoters. The use of sulfated hematite has been shown to yield enhanced conversion for the liquefaction of a subbituminous coal as compared to hematite. Further, the use of promoter metals such as molybdenum and tungsten on the sulfated hematite was shown to further improve the activity of these particles. More recently it has been shown that the addition of combinations of promoters, such as nickel and molybdenum, may increase the activity of the particles at lower promoter loading. The role of the promoter metals on sulfated hematite will be compared to other unsupported catalysts using model compound reactions.

Introduction

The utility of iron based dispersed catalysts in direct coal liquefaction has been well established since the early 1900's, particularly for the liquefaction of low rank coals. Since that time considerable effort has been directed at improving the activity of these catalysts. This effort has focussed on reducing the particle size, enhancing and maintaining the dispersion, and modifying the structure by addition of promoters. Reducing the particle size will increase the surface area to volume ratio and result in higher activity at similar weight loadings. Further, sufficiently small particles may have properties different from those of the bulk, particularly with regard to surface energetics.

The use of oil soluble organometallic precursors offer the highest possible initial dispersion. However, one study found that these precursors tend to agglomerate and form larger particles at a faster rate than a particulate precursor.[1] This agglomeration quickly reduces the high dispersion and associated surface area for the oil soluble precursors. This would seem to indicate that particulate catalysts can maintain high dispersion for longer times and may therefore have higher activities than the organometallic precursors.

Efforts to improve the activity of iron oxide particulate catalysts by reducing the particle size may have reached a limit in the form of Nanocat produced by Mach I. These particles are reported to have an average diameter of 30 Å. The small size of the particles makes identification of the phase difficult by traditional techniques. The Nanocat particles have been identified as α-Fe_2O_3, γ-Fe_2O_3, and FeOOH by the manufacturer and various researchers, respectively.[2,3] These particles have shown improved activity for the liquefaction of a low rank coal.[4]

Several studies have shown the high activity of sulfated hematite for both liquefaction and coprocessing of coal with a petroleum resid.[5,6,7] The use of molybdenum or tungsten as a promoter metal further improved the activity of these particles.[8,9] The use of nickel, cobalt, tungsten, and molybdenum have been examined as promoter metals, both individually and in combination.[10] Molybdenum showed the largest increase in activity when used as a promoter on the sulfated hematite. While the activity of tungsten and cobalt, when used in combination with molybdenum, appeared nearly additive, the combination of nickel and molybdenum exhibited a synergistic

effect, resulting in higher conversions and lower promoter loading.

Unsupported molybdenum carbides and nitrides have been prepared and tested for their activity using model compound reactions.[11 12] The results indicate the significant activity of these particles for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The molybdenum carbide was found to be resistant to bulk sulfidation during the reaction, although it was reported that a surface layer of MoS_2 may have been formed. The sulfided Mo_2N was reported to have higher activity for HDS than either MoS_2 or molybdate indicating that the surface was not MoS_2, although the exact surface composition was not determined.

The role of catalysts in coal liquefaction is obscured by the complexity of the coal molecule itself. The exact nature of the structure of coal has been the object of considerable study. While the structure is not known, it is generally accepted that coal is composed of highly aromatic clusters connected by crosslinking bonds. These crosslinks may consist of aliphatic (methyl or ethyl) bridges or heteroatom (O,S,N) bridges. The role of catalyst in selective cleavage of these bonds may be elucidated by the use of model compound reactions. The activity for cleavage of the sulfur bridges may be studied by the HDS of benzothiophene. Similarly, the activity for cleavage of the etheric bond may be inferred from the HDO of diphenyl ether and the activity for nitrogen removal by the HDN of quinoline.

Experimental

The reactions were carried out using 25 ml stainless steel microautoclave reactors. The reactors were loaded with a 5 wt% solution of reactant in hexadecane. The catalysts were loaded at 5 wt% on reactant basis and 0.017 g dimethyldisulfide (DMDS) was added in most runs. Experiments were carried out using DMDS alone in order to determine its influence on activity and selectivity. The reactors were purged and pressurized to 800 psig (cold) with hydrogen. The loaded reactors were placed in a heated fluidized sand bath at 385°C and agitated vertically at 400 cycles/minute to minimized any mass transfer constraints. The reactions were carried out for times of 15 to 60 minutes after which the reactor was quenched in a cool sand bath.

The reaction products were removed from the reactor by washing with THF. A gas chromatograph (Hewlett Packard 5890 Series 2) using both a 30 m DB-5 and a 30m carbowax column was utilized to analyze the products of the reaction. The activity was determined by the rate of model compound disappearance.

The spent catalyst was collected and stored with the product to reduce oxidation from exposure to air. The major phase of the particles was determined by XRD and the average particle diameter was estimated from the peak broadening using the Debye-Scherrer relationship. This allowed the comparison of catalyst conversion to reaction conversion.

Catalyst Synthesis and Characterization

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. In this study, urea was used to effect the precipitation of ferric ammonium sulfate (iron alum), following the method of Kotanigawa et al.[5] The promoter metal molybdenum was incorporated by addition of ammonium molybdate to the iron alum solution, as described previously.[10] 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 the electron microscopy have shown that the catalysts consist of a loose agglomeration of particles with an acicular shape with average dimensions of ~10x50 nm, shown in Figure 1. Surface areas were

measured by the nitrogen BET adsorption and were found to be in the range of 100-200 m^2/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, shown in Figure 2. The XRD spectra of the as-formed catalyst indicate the major phase is α-FeOOH in addition to a trace of α-Fe also present. After calcination the major phase was α-Fe_2O_3 with α-Fe still present. The relative amount of α-Fe does not appear to be affected by the calcination.

Elemental analysis of the sulfated hematites indicated sulfur contents of 2-6 wt%. It has been reported that the sulfur is present on the surface of the hematite as chemisorbed SO_3. XPS confirmed this showing that the surface sulfur concentration was significantly higher than the bulk concentration. It was found that the sulfur content decreased with increasing molybdenum concentration. This may indicate that molybdenum is chemisorbed as MoO_3 displacing the sulfur on the surface. The XPS studies confirm this, showing 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 are substituted into the iron oxide matrix. 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 substitute.[13]

The molybdenum nitride (Mo_2N), molybdenum carbide (Mo_2C), and molybdenum sulfide (MoS_2) catalysts were produced by a laser pyrolysis technique. This method utilizes the intersection of a tunable CO_2 laser with a gas stream to create a small (~1mm^3) pyrolysis zone. The flow rate of the gases determines the residence time in the reaction zone and, consequently, the particle size and phase. This method has been shown to produce monophasic particles with a narrow size distribution. The particles have an average diameter of ~5 nm and a surface area of 65 m^2/g.

Results

The use of the unsulfided molybdenum promoted sulfated hematite showed little impact on the hydrogenation of naphthalene varying only slightly from the thermal conversion of 7% at 60 minutes. The addition of sulfur alone impacted more favorably on the reaction increasing the conversion at 60 minutes to 19%. The synergism between the sulfur and the promoted sulfated hematites is clear in the experiments using added sulfur with the catalyst. In these runs the conversion increased to 82% at 60 minutes. This corresponds well with other work which has shown that the activity of iron based catalysts is dependent on the partial pressure of H_2S present.[14]

The unsulfided molybdenum nitride, with a conversion of 59% at 60 minutes, showed higher activity for naphthalene hydrogenation than the unsulfided molybdenum promoted sulfated hematite. The addition of sulfur to the molybdenum nitride had only a minor effect on conversion. However, the use of a molybdenum sulfide resulted in a significant increase in conversion to 46% at 30 minutes compared to 29% for the sulfided molybdenum nitride. This indicates that the nitride is stable at these conditions and resists surface sulfidation, agreeing well with previous findings.[12]

The activity of the promoted sulfated hematite for the HDO of diphenyl ether followed a similar trend. The unsulfided molybdenum promoted sulfated hematite showed a slight increase in conversion to 26% at 60 minutes, compared to 21% for the thermal run. The addition of sulfur alone caused a significant decrease in conversion at 60 minutes to 12%. The combination of sulfur and molybdenum promoted sulfated hematite resulted in an increase in conversion to 39% at 60 minutes again due to the attainment of the active phase.

The molybdenum nitride showed a higher activity for HDO than molybdenum promoted sulfated hematite both with and without sulfur. The conversion at 60 minutes was 53%, significantly higher than the 39% achieved with the promoted hematite with sulfur. The addition of sulfur to the molybdenum nitride resulted in a substantial loss of activity yielding a conversion of only 20% at 60 minutes. This indicates that the

addition of sulfur severely inhibits the catalytic activity of the molybdenum nitride.

Conclusions

The activity of promoted sulfated hematite has been compared to the activity of other unsupported catalysts using model compound reactions. Preliminary results indicate that the molybdenum promoted sulfated hematite shows significantly higher activity for the hydrogenation of naphthalene to tetralin when sufficient sulfur is added to the reaction. In the absence of added sulfur the activity of the promoted sulfated hematite was negligible.

The molybdenum nitride exhibits the highest activity for HDO of diphenyl ether. The addition of sulfur increased the activity of the promoted sulfated hematite but severely inhibited the activity of the molybdenum nitride.

In both reactions the catalyst loading was 1 wt% on reactant solution. Since the cost of the promoted sulfated hematite is substantially lower that the molybdenum nitride, due to a lower molybdenum content, the results of this study indicate that significant improvements in process economics may be achieved through the use of these catalysts.

Acknowledgements

The authors would like to gratefully acknowledge support for this project recieved from the United States Department of Energy under contracts DE-AC22-91PC91040 and DE-FC22-93PC93053.

References

1. Djega-Mariadassou, G., *et al. Fuel Processing Technology* **12**, 143-153 (1986).
2. Srinivasan, R., Keogh, R.A. & Davis, B.H. *ASC-Division of Fuel Chemistry Preprints* **38**, 203-210 (1993).
3. Zhou, J., Feng, Z., Huggins, F.E., Shah, N. & Huffman, G.P. *ACS-Division of Fuel Chemistry Preprints* **38**, 196-202 (1993).
4. Anderson, R., Givens, E.N. & Derbyshire, F. *ACS-Division of Fuel Chemistry Preprints* **38**, 495-502 (1993).
5. Kotanigawa, T., Yokoyama, S., Yamamoto, M. & Maekawa, Y. *Fuel* **68**, 618-621 (1989).
6. Pradhan, V.R., Tierney, J.W., Wender, I. & Huffman, G.P. *Energy & Fuels* **5**, 497-507 (1991).
7. Pradhan, V., Tiemey, J.W. & Wender, I. *ACS Preprint - Fuel* **36**, 597-604 (1991).
8. Pradhan, V.R., Herrick, D.E., Tiemey, J.W. & Wender, I. *Energy & Fuels* **5**, 712-720 (1991).
9. Pradhan, V.R., Hu, J., Tierney, J.W. & Wender, I. *Energy & Fuels* **7**, 446-454 (1993).
10. Hager, G.T., Givens, E.N. & Derbyshire, F.J. *ACS-Division of Fuel Chemistry Preprints* **38**, 1087-1092 (1993).
11. Schlatter, J.C., Oyama, S.T., Metcalfe, J.E., III & Lambert, J.M., Jr. *Ind. Eng. Chem. Res.* **27**, 1648-1653 (1988).
12. Markel, E.J. & Zee, J.W.V. *Joumal of Catalysis* **126**, 643-657 (1990).
13. Faure, G. *Principles and Applications of Inorganic Geochemistry* 1-626 (Macmillan Publishing Company, New York, 1991).
14. Sweeny, P.G., Stenberg, V.I., Hei, R.D. & Montano, P.A. *Fuel* **66**, 532-541 (1987).

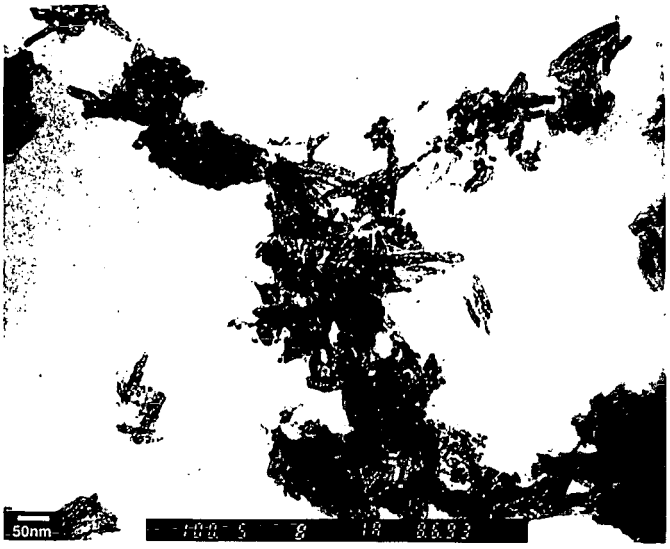

Figure 1. TEM micrograph of molybdenum promoted sulfated hematite

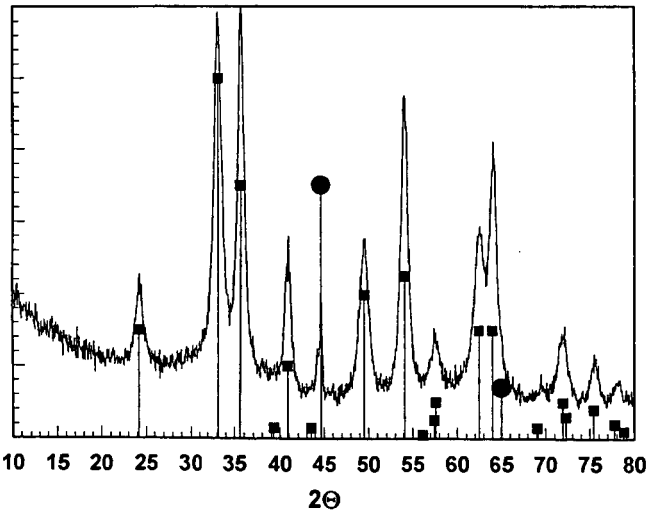

Figure2. XRD spectrum of molybdenum promoted sulfated hematite indicating peaks identified as hematite and α–Fe