

ACTIVITY, CHARACTERIZATION, AND SINTERING BEHAVIOR OF SULFATED IRON OXIDES IN LIQUEFACTION OF LOW PYRITE COALS.

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Abstract

The activity of small amounts of iron and molybdenum added as finely divided sulfated oxide/oxyhydroxide catalysts (FeOOH/SO_4 , $\text{Fe}_2\text{O}_3/\text{SO}_4$ and $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$) for the direct liquefaction of low pyrite bituminous (Blind Canyon) and subbituminous coals (Wyodak) is reported in this paper. The quantification of dispersion and the composition of sulfated iron oxide/oxyhydroxide catalysts before and after coal liquefaction reactions is also reported. Catalytic dispersions (such as surface area and particulate size) were determined for the oxides and oxyhydroxides of iron containing 3-4 wt% of sulfate anion as such and after their transformation from the oxide phase to the sulfides during the course of coal liquefaction. The rates of these transformations were studied at 400°C and information on the size and composition of the resulting sulfide particles was obtained. It was found that the initially added sulfated iron oxides were completely converted to pyrrhotite, Fe_{1-x}S , after only five minutes of reaction at 400°C. Fe_7S_8 , prepared by treating sulfated iron oxide with sulfur in the presence of tetralin, was also used as a catalyst for coal liquefaction and was found almost as effective as the initial sulfated iron oxide. 1000-5000 ppm of iron and 20-100 ppm of molybdenum were used in our catalytic systems with respect to coal. Molybdenum, used in small amounts, was more effective when used with the calcined form of the sulfated iron oxide than with its uncalcined form, FeOOH/SO_4 .

Introduction

Catalysis for direct coal liquefaction (especially for coal dissolution) by highly dispersed catalysts is a topic of considerable interest among researchers in this field^[1]. Application of finely divided and chemically modified powdered solid catalysts, especially those based on cheap and environmentally benign iron, is very promising^[2,4,5]. The objective of our research has been to develop novel catalytic systems based on the sulfate and molybdate anion-promoted oxides/oxyhydroxides of iron which can provide high dispersions and activity for coal liquefaction.

We have synthesized and characterized a number of sulfate-promoted oxides of metals such as Fe, Sn, Zr, Ti, and Hf.^[3] We recently reported on the use of sulfate-promoted iron and tin oxides for the direct liquefaction and coprocessing of Argonne Illinois No.6 coal with tetralin and with Maya ATB heavy oil respectively^[6,7]. The sulfate anion treatment of iron(III)oxides was found to enhance their acidic character and bring about a decrease in the particulate size. Sulfated iron oxides were also found to be active as catalysts at low iron concentrations (3500 ppm with respect to coal) for coal liquefaction. The sulfated iron oxide catalysts were completely converted to highly dispersed (average size = 15 nm) pyrrhotites (Fe_{1-x}S) under coal liquefaction conditions in the presence of enough sulfur.

In this paper, we discuss the properties and activities of a new class of sulfated catalysts. These are based on sulfated oxyhydroxides of iron, FeOOH/SO_4 and $\text{Mo}/\text{FeOOH}/\text{SO}_4$. A comparison is made between the activities of different sulfated iron oxyhydroxides promoted with molybdenum. The effects of small catalyst concentrations (20-100 ppm Mo and 1000-5000 ppm Fe) on conversion levels of a low-pyrite Blind Canyon coal were studied. An attempt was made to characterize the composition and the extent of dispersion of the sulfided catalysts obtained during coal liquefaction reactions. This includes study of the rate at which the initial sulfated metal oxide is converted to the corresponding sulfide under coal liquefaction conditions and also determination of the extent of catalyst particle agglomeration with time at reaction temperature.

Experimental

Catalyst Preparation and Characterization: The sulfated oxides and oxyhydroxides of iron were prepared from either the sulfate, chloride, or nitrate salts precipitated with either ammonia water or urea depending on whether heterogeneous or homogeneous coprecipitation routes were followed. Small amounts of molybdenum (0.5-2 wt% of the iron oxyhydroxides) were introduced into the catalysts by the incipient wetness impregnation technique from an aqueous solution of ammonium heptamolybdate. The catalysts were characterized by BET-surface area analysis, sulfur analysis, thermogravimetry (TGA), acidity measurements, thermal stability measurements, X-ray diffraction, and electron microscopy. The residues of coal liquefaction experiments were also analyzed using X-ray diffraction and a JEOL 2000 FX STEM (100 kV beam) with an energy dispersive X-ray spectrometer (EDX) to determine composition and dispersion information about the catalytic phases formed under liquefaction conditions.

Reaction Studies: The low-pyrite Blind Canyon obtained from the Penn State Coal Research Bank and Wyodak (subbituminous) obtained from the Argonne Premium Coal Sample Bank were used for these studies. Elemental analyses of the two coals are shown in Table 1. Tetralin was used as the reaction solvent (3:1 by weight to coal) and elemental sulfur (2:1 by weight to catalyst) was used for catalyst sulfidation. Coal liquefaction reactions were carried out in both a 300 cc stainless steel autoclave reactor and a 27 cc tubing bomb microreactor. Elemental sulfur was used in excess for sulfiding catalysts in situ. Soxhlet extraction with methylene chloride was used to determine coal conversion. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles (oils) were determined by adding 40 volumes of n-pentane to the methylene chloride solubles and using Soxhlet extraction with n-pentane. Pentane-insoluble but methylene chloride soluble material was referred to as asphaltenes.

Results and Discussion

Catalyst Characterization: Specific surface areas of the sulfated iron oxyhydroxides and oxides, modified with small amounts of molybdenum, were determined by the BET method. In going from the unsulfated oxyhydroxides to the sulfated ones, surface areas increased from about 40 m^2/g to 127 m^2/g . Nitrogen adsorption porosimetry measurements indicated a bimodal distribution of the pores (essentially the void spaces between the primary crystallites). X-ray diffraction line broadening measurements and transmission electron microscopy indicated the particle size of the oxyhydroxides to be between 15-20 nm. The particles were elongated and needle-shaped. Differential thermal analysis studies of the sulfated oxyhydroxides indicated that crystallization to

the oxides occurred above 450°C. The presence of small amounts of the sulfate group in the oxyhydroxides, thus, delayed the crystallization (and therefore crystal growth) by about 150°C. Sulfated oxyhydroxides also exhibited a significant chemisorption of pyridine at high temperatures indicating a strong surface acidic character. A summary of catalyst properties is given in Table 2; the uncalcined sulfated iron oxyhydroxide has a specific surface area higher than its calcined form, sulfated iron oxide. The molybdate anion (MoO_4^{2-}), added in small amounts (3 wt% of the oxide), exhibits a similar influence on the catalyst properties as does the sulfate anion.

Reaction Studies:

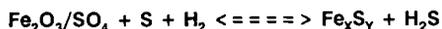
1. Effect of Reaction Temperature : The following three catalytic systems were used for the liquefaction of Argonne Wyodak coal (0.17 % pyrite) at different temperatures to determine the qualitative effect of reaction temperatures on the activities of these catalysts for coal conversion: $\text{Fe}_2\text{O}_3 + \text{S}$, $\text{Fe}_2\text{O}_3/\text{SO}_4 + \text{S}$, and $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4 + \text{S}$. As shown in Figure 1, the activities of sulfated catalysts for the production of oils (n-pentane solubles) from coal increased proportionately in going from 375 to 425°C.

2. Sulfated Iron Oxyhydroxides and Molybdated Iron Oxide : The FeOOH/SO_4 and $\text{Fe}_2\text{O}_3/\text{MoO}_4$ catalysts resulted in comparable levels of coal conversion to n-pentane solubles as did the sulfated iron oxide for the liquefaction of Wyodak coal (Figure 2) under similar reaction conditions. From these results we see that the effect of anions in modifying the catalytic properties of transition metal oxides is not anion-specific so long as the modifying anion is held by the oxide surface strongly even at high temperatures. The effect of adding sulfuric acid separately with the unsulfated iron oxide was not the same as that of previously sulfated iron oxide. The combination of pure iron oxide and dilute sulfuric acid resulted in a slightly higher conversion values than the iron oxide alone, but these conversions were lower than those obtained with presulfated iron oxide.

3. Effect of Iron and Molybdenum Catalysts Loadings on Liquefaction of Low-Pyrite Blind Canyon Coal : In order to study the effect of small catalyst loadings on coal conversion levels, it was necessary to use a coal containing as low an amount of pyritic iron as possible. For this reason, Blind Canyon coal was chosen for these studies. Sulfated iron oxyhydroxide, which was found as active as the sulfated iron oxide catalyst, was employed as catalyst for the runs carried out to determine the effect of small loadings of iron on coal conversion (1000-5000 ppm with respect to coal). The results are shown in Figure 3. It can be noted from Figure 3 that the catalytic effect of added iron (as 15 nm size FeOOH/SO_4 catalyst) becomes significant only above 2500 ppm of iron with respect to coal. The incorporation of small amounts of molybdenum into this sulfated oxyhydroxide ($\text{Mo}/\text{FeOOH}/\text{SO}_4$) was not as effective for coal conversion as that in the sulfated iron oxide ($\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$). The lack of high molybdenum dispersion due to the absence of a calcination treatment for the earlier catalyst might be part of the reason for its lower activity as compared with the calcined catalyst, $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$. The effect of molybdenum loadings between 20-200 ppm (with respect to coal) added with 2500 ppm Fe as $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$ is shown in Figure 4. Additional amounts of molybdenum in an already active sulfated iron oxide do not bring about significant enhancement in total coal conversions (conversions increase from about 75 % in the absence of Mo to about 80 % in its presence), but the yield of light oil (n-pentane soluble products) is significantly enhanced in the presence of small amounts of Mo. This suggests that

molybdenum, due to its strong hydrogenation function (in the form of MoS_2), helps to produce more oil at the expense of the asphaltenes.

Catalyst Transformation and Sintering Studies: It is well understood now that any iron-based catalyst precursor added at the beginning of coal liquefaction is converted to iron sulfides in the presence of enough sulfur under liquefaction conditions. The quantification of sulfided phases, thought to be catalytic, is essential for the understanding of the mode of action of the iron-based catalysts. We have made an attempt to investigate the rate of transformation (i.e. compositions of sulfides formed at different reaction times) and the extent of catalyst sintering (i.e. the degree of catalyst dispersion) of the iron-containing phases that result from addition of sulfated iron oxides during coal liquefaction. In general, the stoichiometry (or composition) of the iron phases formed during liquefaction is controlled by the following equation:



The objective here is to determine the atomic ratio (Fe/S) and the grain sizes of the iron-phases in the coal liquefaction residues using analytical tools such as X-ray diffraction and electron microscopy. The composition of the catalysts (sulfated and sulfided phases) and their sizes have been studied at different reaction times using the following model systems:

- (I) Active carbon + tetralin + $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst
- (II) Tetralin + S + $\text{Fe}_2\text{O}_3/\text{SO}_4$ (Presulfidation)
- (III) Low-pyrite Blind Canyon coal + S + finely divided iron catalysts + tetralin

Active carbon was used instead of coal to avoid interference due to the mineral matter from coal. The reactions were carried out under identical conditions as coal liquefaction with the addition of elemental sulfur for metal sulfidation. When the reactions were carried out with a sulfated iron oxide catalyst for different reaction times, it was found that the initial sulfated iron oxide takes about five minutes at reaction temperature to convert completely to the sulfided iron phases, i.e., pyrite and finally pyrrhotites. The grain size changes occur primarily during this transformation. No further changes (increases) in the grain size of iron-containing phases was observed even when the reaction was carried out for two hours. The initially added sulfated iron oxide catalyst (particle size = 20 nm) were converted completely to pyrrhotite after five minutes of reaction (particle size = 10-50 nm). A similar transformation picture was seen when a soluble precursor of iron, $\text{Fe}(\text{CO})_5$ was used. Figure 6 shows the transmission electron micrographs of the sulfated iron oxide before and after reaction treatment as in the model system (II) indicated earlier. As shown in Figure 5, all of the initial sulfated iron oxide had been converted to pyrrhotites, primarily, Fe_7S_8 . There was no apparent increase in the grain size during this high temperature transformation. Figure 6 compares the particle sizes of the sulfided iron catalysts derived *in situ* from FeOOH/SO_4 and $\text{Fe}(\text{CO})_5$ precursors during direct liquefaction of Blind Canyon coal. The results of catalyst size and composition studies obtained using the model system (I) followed by examination of the residues by XRD, TEM, and EDX, are summarized in Table 3. Complete transformation of the initially added sulfated iron oxide catalyst to pyrrhotite occurred after five minutes at reaction temperature. The grain size change associated with this phase change was observed by electron microscopy, while particle sizes of the sulfided phases essentially remained the same without much further agglomeration or sintering for two hours of reaction time.

Conclusions

The increase in total conversion as well as the increase in conversion to oils obtained with sulfated oxides is attributed primarily to enhanced "dispersion" (surface area/gm) with possibly a small contribution, made early on, from the high surface acidity of these oxides. Due to increase in the specific surface area and decrease in the average particle size of the oxides upon addition of small amounts of the sulfate group, conversion of the oxides to active catalytic sulfide phases, especially to non-stoichiometric sulfides of iron, is facilitated. More of the active catalyst surface of these sulfides becomes available for reaction and catalyst agglomeration is decreased. Sulfated iron-based finely divided catalysts result in better catalytic dispersion than soluble precursors such as $\text{Fe}(\text{CO})_5$. Addition of small amounts of molybdenum to the sulfated iron oxides increases its activity, especially for the production of oils.

References

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Table 1. Elemental Analyses of Coals (All in weight percents)

Coal	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Pyritic Sulfur
Wyodak	75.0	5.4	1.1	18.0	0.5	0.17
Blind Canyon	81.6	6.2	1.4	10.3	0.5	0.02

Table 2. Summary of Catalyst Characterization Before Reaction

Catalyst	Wt % SO ₄	Surface Area, m ² /g	Average Size, nm (XRD)	Average Size, nm (TEM)
Fe ₂ O ₃	0.0	26.8	46	65
Fe ₂ O ₃ /SO ₄	3.4	81.7	12	20
Mo/Fe ₂ O ₃ /SO ₄	3.1	81.5	12	20
FeOOH/SO ₄	10.2	127.0	12	25
Fe ₂ O ₃ /MoO ₄	0.0	88.0	09	15

Table 3. Results of Catalyst Transformation and Sintering Studies on Model System (I)

Reaction Time	Iron-Phases Detected	Average Particle Size (XRD)	(Fe/S) Atomic Ratio
0 min.	Fe ₂ O ₃ , Fe ₃ O ₄ , FeS ₂ , Fe _{1-x} S	14 nm	1.4
30 min.	Fe ⁰ , FeS ₂ , Fe _{1-x} S	16 nm	1.0
120 min.	Fe _{1-x} S	16 nm	0.9

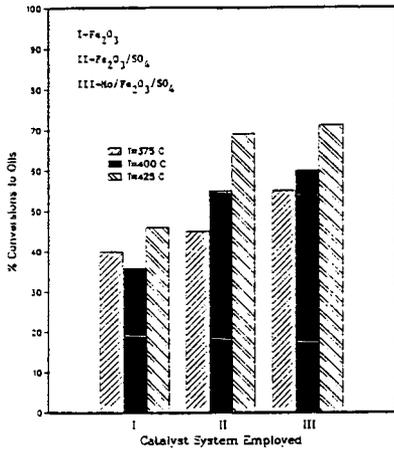


Figure 1. Activity of Sulfated Catalysts for Direct Liquefaction of Wyodak Coal at Three Reaction Temperatures

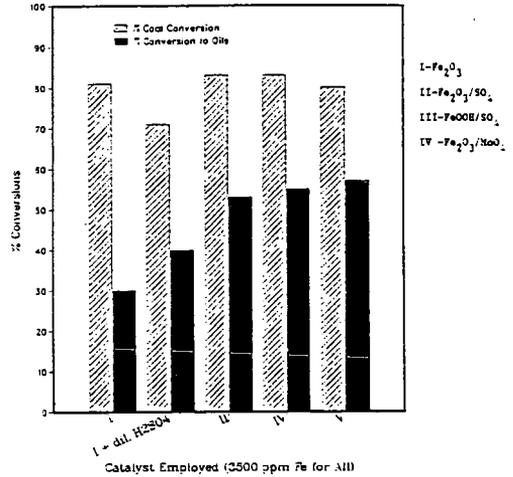


Figure 2. Activity of Oxyhydroxide and a New Molybdated Catalyst for Liquefaction of Wyodak at 400°C

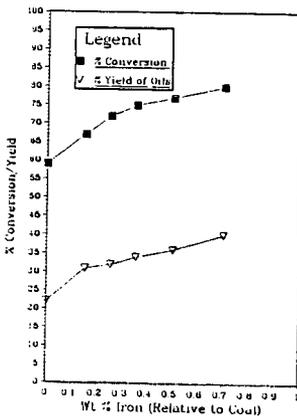


Figure 3. Conversion of Blind Canyon vs. Iron Concentration at 400°C

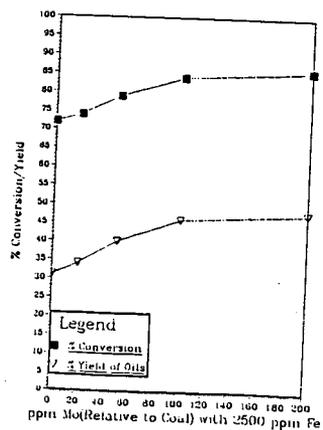


Figure 4. Conversion of Blind Canyon vs. Molybdenum Concentration at 400°C

Before Reaction-

Size = 20 nm

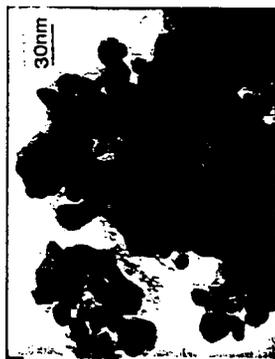


After Reaction-

Size = 20 nm

Fe_7S_8

$Fe_{11}S_{12}$



From $FeOOH/SO_4$

size = 10-25 nm



From $Fe(CO)_5$

size = 20-50 nm

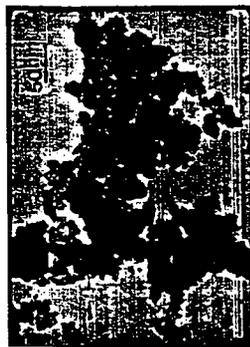


Figure 5. Sulfated Iron Oxide Catalyst: Before and After Sulfidation Reaction.

Figure 6. Dispersion of Fe-Containing Particles after Coal Liquefaction Reaction using Two Different Precursors.