

SULFATED AND MOLYBDATED IRON (III) OXIDE CATALYSTS IN COAL LIQUEFACTION

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INTRODUCTION

Iron, because of its low cost, activity, and environmental acceptability, has been perceived as a potential catalyst for the first stage of coal liquefaction, namely coal dissolution. A chief objective of various methods of adding iron catalysts is to provide high catalytic surface area and fine particulate size. The initial dispersion of the precursor has a strong influence on the activity of the sulfided phases formed under liquefaction conditions. Means must also be sought to prevent agglomeration of catalyst particles so as to maintain their state of high dispersion. In the presence of enough sulfur, iron catalysts form pyrrhotites ($Fe_{1-x}S$) which, along with hydrogen sulfide, function as catalysts for the hydrogenation and hydrogenolysis reactions which occur during the hydroliquefaction of coal^{1,2,3}. Application of finely divided and chemically modified powdered solid iron oxide based catalysts used in this work shows considerable promise⁴. These catalysts have initial sizes in the nanophase region (1-100 nm); their ultrasmall size allows them to have dramatically different properties.

The objective of this research has been to use low-sulfur, low-pyrite coals to verify the catalytic effects of small amounts of iron added to the liquefaction reactor as sulfate and molybdate anion-promoted oxides or oxyhydroxides. We have 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, respectively⁴.

The following topics will be discussed: (i) activity of small amounts of iron and molybdenum added as sulfated oxides for direct liquefaction of low pyrite coals (hvbc Blind Canyon, 0.01 wt% pyrite, and subbituminous Wyodak with 0.17 wt% pyrite), (ii) synthesis and physicochemical properties of sulfated and other anion-modified iron oxide/oxyhydroxide catalysts before use in coal liquefaction reactions, (iii) quantification of dispersion and composition of iron phases after coal liquefaction and (iv) transformation and sintering behavior of these catalysts under coal liquefaction conditions.

EXPERIMENTAL

Starting Materials. The hvbc Blind Canyon DECS-17 coal was obtained from the Penn State Coal Sample Bank and the Wyodak subbituminous coal from the Argonne Coal Sample Bank. Elemental analyses are given in Table 1. Starting materials for catalyst preparation were iron alum [$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$], ferric nitrate, urea, and 28% ammonia water. Ammonium heptamolybdate and ammonium metatungstate were purchased from the Sigma Chemical Co. and from Strem Chemicals, Inc. respectively.

Catalyst Preparation and Characterization. The sulfated oxides and oxyhydroxides of iron were prepared from either the sulfate or

nitrate salts using urea or NH_4OH as the precipitating agents, added dropwise so that the pH of the solutions changed with time. The result of the hydrolysis reaction is formation of iron oxyhydroxide (FeOOH) with small residual amounts of sulfate anion adsorbed on the surface. The presence of sulfate anions during precipitation has been reported to bring about surface charge modifications of the precipitated particles; this affects the chemistry and kinetics of the precipitation/crystallization. The catalysts used in this study were Fe_2O_3 (I), $\text{Fe}_2\text{O}_3/\text{SO}_4$ (II), $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$ (III), FeOOH/SO_4 (IV), $\text{Fe}_2\text{O}_3/\text{MoO}_4$ (V), $\text{Fe}_2\text{O}_3/\text{WO}_4$ (VI) and $\text{Mo}/\text{FeOOH}/\text{SO}_4$ (VII). These catalysts were prepared by modification of the procedure used for the preparation of $\text{Fe}_2\text{O}_3/\text{SO}_4$ (II)⁴.

The following measurements were made to characterize the size and structure related properties of these catalysts: BET surface area, sulfur content, thermogravimetry (TGA), acidity measurements, thermal stability measurements, X-ray diffraction and electron microscopy. Residues of coal liquefaction experiments were also analyzed using a Phillips X-ray diffractometer and a JEOL 2000 FX STEM (100 kV beam) with an energy dispersive X-ray spectrometer (EDX) to determine composition and dispersion of catalytic phases formed under liquefaction conditions.

Reaction Studies. Tetralin was the reaction solvent (3:1 by weight to coal) and elemental sulfur (2:1 by weight to catalyst) was used for *in situ* catalyst sulfidation. Although a donor solvent such as tetralin tends to mask catalytic effects in coal conversion, its presence during coal liquefaction ensures complete conversion of the iron catalyst precursor to its sulfide via H_2S formation in 5-6 minutes at 400°C at 1000 psig cold H_2 . Coal liquefaction reactions were carried out in both a 300 cc stainless steel autoclave and a 27 cc tubing bomb microreactor at 400°C and 1000 psig ambient H_2 (1800 psig at reaction temperature). Coal conversions were determined using Soxhlet extraction with methylene chloride; soluble products were recovered by evaporation at 45°C under vacuum. Pentane solubles (oils) were determined by Soxhlet extraction of the methylene chloride solubles with n-pentane. Asphaltenes are the pentane-insoluble but methylene chloride soluble material.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization. The catalysts used are listed in Table 2 with relevant physicochemical properties. The presence of sulfate anions during precipitation was necessary to form nano-sized oxide particles which were resistant to agglomeration at high temperature.

The measure of initial dispersion of the catalysts was obtained using XRD line broadening measurements and transmission electron microscopy (TEM). The crystallite sizes of sulfated iron oxyhydroxides could not be determined by X-ray diffraction due to their low bulk crystallinity. These oxyhydroxides, after calcination, gave rise to catalyst II (high bulk crystallinity). Use of TEM revealed that catalyst IV contained very small needle-shaped, elongated, thin crystallites with average dimensions of 30 x 3 nm. Nitrogen porosimetry measurements were carried out on all catalysts. A macroporous distribution of pores was obtained for catalyst IV, indicating that individual fine particles come together to form very thin channels with average dimensions of 20-30 nm. All calcined iron oxides, completely crystalline after calcination, were 10-15 nm and

were elongated in shape as determined by electron microscopy.

The uncalcined sulfated oxyhydroxides such as IV had BET specific surface areas (120-130 m²/g) higher than the calcined oxides (80-90 m²/g). Evidence that all of the sulfated iron oxides had low porosities with pore volumes smaller than 0.2 cc/g was obtained by calculating equivalent spherical diameters from their surface area values and comparing them with diameters obtained by TEM. The values agreed within 10%.

The iron oxide surfaces were studied by FTIR and XPS. The FTIR spectrum of catalyst IV, obtained at 450°C under vacuum, showed an S=O band at 1440 cm⁻¹ similar to the S=O bonds formed in the bidentate chelating complex of sulfate anion with an oxide surface proposed by Tanabe et al.⁵ Upon adsorption of pyridine, this band shifted to about 1500 cm⁻¹ and new bands, corresponding to coordinatively bonded pyridine (Lewis acid sites) and to pyridinium ions (Bronsted acid sites) appeared in the spectrum. XPS of the sulfated and molybdated iron oxides indicated that almost 95% of the S and Mo, both in 6+ oxidation states, were on the catalyst surface.

Reaction Studies. Coal liquefaction reactions were carried out both in a horizontally shaken tubing microreactor and a well-stirred 300 cc batch autoclave. Blank (thermal) runs were made with a previously unused microreactor to determine the catalytic activity of inherent mineral matter in the coals. Runs were also made with only elemental sulfur added to the reactor without added catalyst. Catalysts were mixed with the coal-tetralin slurry by manual stirring after being preheated in an oven at 450°C for one hour. Liquefaction experiments with sulfated iron oxides, presonicated in the reaction solvent for one hour, were also carried out; this treatment ruptured the catalyst agglomerates (about 1 nm as determined by light scattering) into smaller particles which formed a stable colloidal suspension in tetralin, thereby increasing the extent of initial catalyst dispersion.

Comparison of Catalytic Activities of Sulfated Iron Oxides and Oxyhydroxides with other Finely Divided Catalyst Precursors. Use of catalysts IV and VII (both uncalcined) resulted in total coal conversion levels similar to those obtained with their calcined forms (II and III), although higher oil yields were obtained with the calcined forms. The higher activity of calcined iron oxides for oil production is probably related to their calcination treatment at 500°C for three hours. The higher water content of the oxyhydroxides may make them more susceptible to sintering during transformation to pyrrhotites.

Activities of sulfated iron oxides were compared with those of organometallic precursor complexes such as Fe(CO)₅ and Mo(CO)₆ as well as with a fine divided (30 Å) iron oxide catalyst. Catalyst II was more active than Fe(CO)₅ at the same iron loading. Interestingly, 500 ppm of Mo (added as either Mo(CO)₆ or molybdenum naphthenate) relative to coal resulted in about the same conversion levels as 3500 ppm of Fe added as catalyst II.

Coal Conversion and Oil Yields as a Function of Catalyst Concentration. Coal conversions were carried out using the smallest catalyst loadings that gave meaningful results. Since most coals contain considerable amounts of iron as FeS₂, it is difficult to obtain reliable data on the effect of small catalyst loadings on coal conversion levels. Two coals with low levels of iron, a Blind Canyon

coal with 0.02 wt% of pyrite and a Wyodak coal with 0.17 wt% of pyrite were selected to minimize the effect of inherent mineral matter. Uncalcined catalyst IV, which was as active as the calcined catalyst II, was employed for runs carried out to determine the effect of small loadings of iron (1000-5000 ppm with respect to coal) on coal conversion and on oil yields. With the Blind Canyon coal, a thermal blank conversion of 60% (maf) and oil yield of 22% were obtained. With 3500 ppm of Fe as catalyst II, conversion increased to 77% and oils to 35%. The highest conversion (87% with 48% oils) was achieved with 1% of FeOOH/SO_4 (IV).

The effect of Mo loadings (20-200 ppm with respect to coal) used with 2500 ppm of iron as III was investigated. Very small amounts of Mo added to II enhanced coal conversion from 72% to 80%; the yield of oils, however, rose from 32% without Mo to 46% with 100 ppm of Mo. On increasing Mo loading to 200 ppm, total conversion was 87% and yield of oils 52%. The molybdenum in catalyst III probably forms MoS_2 , which has a strong hydrogenation function so that more oil is produced at the expense of asphaltenes.

Effect of Different Anionic Modifications of Iron (III) Oxides on Coal Liquefaction Activity. Iron oxides modified with 5 wt% of molybdate (MoO_4) or tungstate (WO_4) anions were as active as sulfated iron oxide catalysts in terms of overall coal conversion.

All runs with the Blind Canyon coal were made with addition of elemental sulfur to the reactor. Use of S alone in a blank run (no catalyst added) resulted in 66% coal conversion with 27% oils. Iron oxides modified with either tungstate or molybdate anions resulted in slightly higher oil yields than the sulfated iron oxide. The higher activity is due to formation of highly active and well dispersed MoS_2 or WS_2 . These new types of anionic modifications of iron oxides bring about significant enhancement in coal liquefaction activity.

Catalyst Presulfidation and Re-use. To establish the activity of highly dispersed pyrrhotites formed from the sulfated iron oxides, we carried out presulfidation instead of *in situ* sulfidation of the catalysts by reacting them with 2:1 (by weight) of S in the presence of tetralin at 400°C and 1000 psig H_2 cold for 30 minutes in the 300 cc autoclave. X-ray and electron diffraction indicated that all sulfated iron oxides were converted to Fe_7S_8 with traces of $\text{Fe}_{11}\text{S}_{12}$. X-ray line broadening measurements and transmission electron microscopy indicated a crystal size of 20 nm for these preformed pyrrhotites, which, interestingly, contained 3 to 5 wt% of carbon derived from the solvent tetralin. The tetralin was found to have been hydrocracked, hydrogenated, and dehydrogenated during presulfidation of the sulfated catalysts.

The preformed pyrrhotites were then employed as catalysts for direct liquefaction of Blind Canyon coal at 400°C at 0.25 to 0.35 wt% iron loading relative to coal both with and without added S. The preformed Fe_7S_8 was almost as active as catalyst IV at 0.35 wt% iron. Further addition of S to Fe_7S_8 improved its activity, yielding 42% oils compared to 30% with larger amounts of Fe_7S_8 in the absence of added S with 2500 ppm of iron. Increase in oil yields upon addition of S to Fe_7S_8 indicates possible interactions between pyrrhotites and H_2S for catalyzing hydrogenolysis/hydrogenation reactions during coal liquefaction. The presence of H_2S also ensures that the iron-deficient and sulfur-rich stoichiometry of pyrrhotites is maintained.

Effect of Reaction Temperature. Catalysts I, II and III were used for liquefaction of WyodaK coal at 375, 400, and 425°C. The activities of these catalysts for production of oils from coal increased on going from 375 to 425°C except for the Fe₂O₃ (I) catalyst, for which oils decreased somewhat. Sulfated catalysts resulted in higher yields of oils than the unsulfated ones at all temperatures.

Dispersion and Composition of Catalysts after Coal Liquefaction. To study what happened to initially added iron catalyst precursors after coal liquefaction, we carried out reactions of Blind Canyon coal with II and with Fe(CO)₅. The insoluble residues containing transformed iron catalysts were characterized by X-ray diffraction and STEM coupled with an Energy Dispersive X-ray Detector. The added iron for both precursors was completely converted to pyrrhotites, highly dispersed in the insoluble organic matter in the liquefaction residue. Pyrrhotites formed from Fe(CO)₅ were larger (30-50 nm) than those from II (15-20 nm).

CONCLUSIONS

1. Sulfated iron oxides and oxyhydroxides and molybdenum promoted sulfated iron oxide were active for converting low pyrite coals to liquids at 400°C; coal conversion levels greater than 75%, compared to 66% without catalyst, were obtained with iron loadings between 2500-5000 ppm relative to coal.

2. The sulfate, molybdate and tungstate anions modified the physicochemical properties of iron(III) oxides in a similar way and were about equally effective for direct liquefaction of low-pyrite Blind Canyon coal, but slightly higher yields of oils were obtained with iron oxides promoted by molybdate or tungstate.

3. Uncalcined sulfated iron oxyhydroxides were almost as active as the calcined sulfated iron oxides, but somewhat higher amounts of oils were obtained using calcined oxides. Although initially both oxides and oxyhydroxides are highly dispersed, sulfated oxides resist sintering at high temperatures. Uncalcined sulfated oxyhydroxides have residual moisture which is probably responsible for agglomeration under coal liquefaction conditions.

4. Iron, in the form of sulfated oxides, is completely converted to highly dispersed pyrrhotites within a few minutes at 400°C. These have a composition of Fe₇S₈ and an average particle size of 20 nm. No growth in particle size during reaction was observed. The presulfided Fe₇S₈ is also active for direct liquefaction of coal in the presence of added sulfur.

5. A catalyst system based on anion-modified iron oxides has an initial fine size and a unique ability to resist agglomeration at higher temperatures.

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Table 1. Ash-free Elemental Analyses of Coals (weight percent)

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	0.002

Table 2. Catalyst Characterization before Reaction

Catalyst ¹	Wt % SO ₄	Surface Area, m ² /g	Average Size, nm		
			XRD	TEM	ESD ²
I	0.0	26.8	46	65	41
II	3.4	81.7	12	20	14
III	3.1	81.5	12	20	14
IV	10.2	127.0	nd	16	11
V	0.0	88.0	9	15	13
VI	0.0	91.5	7	15	12
VII	9.8	120.5	nd	20	11

1. Molybdated and tungstated iron (III) oxides contained 5 wt% molybdate or tungstate.
2. ESD is the equivalent spherical diameter of the catalyst particles, calculated from the BET surface area and assuming zero porosity.