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FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

Final Technical Report

by

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1.0 EXECUTIVE SUMMARY

In an effort to develop new disposable catalysts for direct coal liquefaction, several types of clay-supported pyrrhotite catalysts were prepared and tested. These types included iron-pillared (intercalated) montmorillonite, mixed iron/alumina-pillared montmorillonite, iron-impregnated montmorillonite, and iron oxometallate-impregnated montmorillonite. Iron-pillared montmorillonite catalyst precursors were initially prepared by exchange of triiron clusters on fine particles of sodium montmorillonite. Agglomeration occurred with collection and sulfidation to give micron size particles, but good hydrocracking, hydrogenation, and liquefaction activity were retained. Brönsted sites on the clay were active, but the acid-catalyzed retrogressive condensation reactions normally caused by clays were prevented by the iron sulfide.

Several methods for preparing mixed iron/alumina pillared montmorillonites gave highly active catalysts. Mixed pillared clays had more stable surface areas than iron-pillared clays. Hydrogenation and hydrocracking of pyrene was comparable to that observed with zeolites and zinc chloride. Liquefaction with Wyodak coal with 10% of the iron/alumina pillared clay catalyst containing 8 wt% iron gave improved conversions to heptane solubles (53%) compared with thermal (48%). Use of acid-exchanged Wyodak showed a small improvement in conversions. Liquefaction of Blind Canyon coal gave 37% conversion to heptane-solubles, compared with 33% for thermal reaction.

Methods were developed for catalyst testing with a solubilized high molecular weight coal-derived intermediate, the low-severity product from Wyodak coal (LSW). This procedure eliminates mineral effects on catalysts and retrograde reactions, and oils yields can be easily determined. Catalytic hydrogenation of LSW with the iron/alumina-pillared clay for 3 hr gave 47% conversion of asphaltenes to heptane solubles, compared with 26% thermal and 67% with Co-Moly catalyst.

Iron hydroxyoxide-impregnated montmorillonites were prepared from acid-washed montmorillonite using either ferric nitrate or triiron clusters. Because of the highly dispersed iron sites on the acidic clay surface, these unpillared precursors gave highly active catalysts for hydrocracking, hydrogenation, and coal liquefaction after sulfidation. Liquefaction with Wyodak coal with the sulfided catalyst from the ferric-impregnated clay gave a high conversion to heptane solubles (67%), similar to Co-Moly catalyst. Acid-exchanged Wyodak gave improved conversion to heptane solubles (69%). Catalytic hydrogenation of LSW (3 hr) gave 56% conversion of asphaltenes to heptane solubles, compared to 67% with Co-Moly. Thus, the most effective catalysts are those with iron sulfide on a large surface area (fine particles) of an acidic support. The combined effects of clay acidity and hydrogen activation by the highly dispersed iron sulfide resulted in high conversions in hydrocracking and hydrogenation tests. The presence of the fine iron sulfide resulted in minimal coking and condensation reactions.

Iron oxoaluminate and iron oxotitanate were also supported on montmorillonite. These precursors gave catalysts with moderate activities for hydrocracking and hydrogenation. The catalyst from the iron oxotitanate precursor gave excellent conversions of Wyodak coal (98% THF solubles, 59% heptane solubles). These results indicate that the presence of a stabilizing matrix around the iron sulfide is important to high catalytic activity.

Mossbauer spectroscopy was used at several temperatures to determine the forms of the iron present on the highly active catalysts derived from ferric and triron impregnation of the acid-washed montmorillonite. The 4.5°K spectrum indicated that the predominant iron sulfide form was griegite. The other iron present was an oxidic ferrous form probably incorporated in to the clay structure. Based on the temperature dependence, the griegite particles were extremely small. It is possible that the formation of griegite on the clay surface is unique for catalytic forms of iron sulfide.

2.0 GOALS AND OBJECTIVES

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage of the coal macromolecules and removal of oxygen, nitrogen, and sulfur heteroatoms. The goal of the project research was to develop new catalysts for the direct liquefaction of coal. This type of catalyst consists of fine clay particles that have been treated with reagents which form pillaring structures between the aluminosilicate layers of the clay. The pillars not only hold the layers apart but also contain active catalytic sites for hydrogenation of the coal and the solvent used in the liquefaction. The active catalytic sites are composed of iron sulfides, which have been previously demonstrated to be active for coal liquefaction. The active sites are generated in situ by sulfiding the corresponding oxyiron species. The size of the catalyst will be less than 40 nm in order to promote intimate contact with the coal material. Since the clays and reagents for pillaring and activating the clays are inexpensive, the catalysts can be discarded after use, rather than regenerated by a costly process.

The project evaluated methods for preparing the fine particle iron/clay dispersions and for activating the particles to generate the catalysts. Characterization studies of the activated catalysts were performed. The effectiveness of the iron/clay dispersion for hydrogenation and coal liquefaction was determined in several types of testing.

3.0 ACCOMPLISHMENTS

3.1 INTRODUCTION

The development and testing of disposable fine particle heterogeneous catalysts for hydrotreating of coals was conducted in this project. These catalysts consist of sulfided iron clusters dispersed on or intercalated into smectite clays. The smectite clays are swelling

phyllosilicate minerals, commonly found as components of soils and sediments and often found as large, mineralogically pure deposits (1). These materials are highly useful in many chemical applications, because of their small particle size (<2 micrometers) and appreciable surface area for the adsorption of organic molecules and unique intercalating capabilities. Hence they are used for supporting microcrystalline or metal cluster catalytic sites. Acid-modified smectites were used for a number of years as petroleum cracking catalysts in the Houdry process, giving gasoline in high yields (1). In the mid 1960's they were replaced by more thermally stable and selective zeolite catalysts.

The advantages of two dimensional chemistry in the interlayer space of the clay structure have recently been investigated. One of the major themes is the intercalation of metal complex catalysts between the aluminosilicate layers. An improvement in catalytic specificity relative to homogeneous solution can be achieved by mediating the chemical and physical forces acting on interlayer reactants. The use of large stable cations to pillar the aluminosilicate layers results in the formation of porous networks analogous to zeolites. In these pillared clays, intercalation of hydroxylated or complexed metal cations maintains the clay layer structure after loss of water and generates a large micropore dimension. These structures are stable up to 450 to 500°C in contrast to the nonpillared clays which dehydrate and collapse at temperatures over 200°C. Acid zeolites are more stable at high temperatures; however, their pores are too narrow to be useful for coal macromolecules. The advantage of the pillared clay catalyst over the zeolites is that pore size can be controlled and made larger than those of the zeolites, and hence are more suitable for the adsorption of coal macromolecules. Therefore, these pillared clay catalysts may be more effective in cracking coal macromolecules than the conventional catalysts. The intent of this work is to discover how to finely disperse the iron sulfide catalytic sites in the pillared clay structure.

The sodium form of montmorillonite disperses to an extremely fine particle size in an aqueous medium with low concentrations of base. This form is preferred for the metal ion exchange reaction that gives the intercalated clay, since the clay layers are highly separated in this state and mass transfer is rapid. At this point the iron metal is highly dispersed as intercalated polyoxymetal cations. The iron-exchanged clay was subsequently calcined to form the iron oxide pillars. We expected at this point that the iron would still be highly dispersed as pillars. It is likely, however, that calcining affected not only the size of the clay particles, but also the particle size of the iron clusters within the clay layers. The forms of iron present after intercalation, calcining and sulfidation need to be better understood. The relationship between preparation methods, starting materials (clay type and iron type), initial particle sizes, and resulting catalytic activities were investigated.

3.2 RESULTS AND DISCUSSION

3.2.1 Iron-Pillared Clays

Preparation methods for iron-pillared montmorillonites were initially investigated. Sodium montmorillonite disperses to an extremely fine particle size in an aqueous medium with low concentrations of base. The clay layers are separated (dispersed and deflocculated) in this state and mass transfer is rapid, thus this form was preferred for metal ion exchange reactions for producing the intercalated clays. The monocationic polyoxytriiron (III) complex (heptaacetatohydroxytriiron nitrate) was exchanged for the interlayer cations of the dispersed sodium montmorillonite (2). The exchange of polyoxytriiron for sodium resulted in a change in particle-size distribution, with a substantial portion of larger particles being formed by flocculation of the very fine particles. Light scattering determination of the particle size gave an average particle size greater than 1 micron. Low-speed centrifugation gave a larger particle fraction (78%), and a fine particle fraction was isolated by high-speed centrifugation.

Calcination of the two iron-exchanged clay fractions gave the stable polyoxyiron cation-pillared clays, which were the precursors for the iron sulfide catalysts. X-ray diffraction studies of both calcined catalyst precursor fractions showed that hematite and maghemite (both Fe_2O_3) had formed. The material from the fine clay particles contained hematite in greater abundance than that from the larger particles. The formation of these different compositions during the calcination of the iron-exchanged clays may be attributed to partial hydrolysis of the triiron clusters during washing and collection procedures. The fine particles were exposed to water for a much greater period of time. These data appear to be similar to those obtained by Lee and others (3) for pillaring with hydrolyzed ferric chloride, which indicated that hematite particles had formed. The d_{001} peak corresponding to the interlayer spacing was present, but was quite broad in the 2θ plot for both samples, indicating that spacings are irregular in the calcined products. Thus, the exchange of the triiron complex results in both oriented aggregation to form pillared structures, but also flocculation to large particles with irregular edge-to-face and edge-to-edge associations of the pillared structures.

When a more rapid method for centrifugation of the fine particles was employed, the X-ray diffraction data showed that the calcined clays from the fine particles had a much smaller amount of hematite than the clay prepared by the former method. Thus, the iron oxide compositions of catalyst precursors obtained from both the fine and larger particles in this preparation were very similar.

Conversions of the oxyiron-intercalated clays to active sulfide forms were performed by various methods. Sulfidation was carried out either by heating the calcined precursor with a mixture of H_2S (100 psi) and H_2 (900 psi) in the rocking heater at 400°C for 2 hr or by in situ reaction with 40 mg of carbon disulfide that was added with the test compound, decalin solvent, or coal, depending on the reaction being carried out. The catalysts prepared by treatment with H_2S exhibited major peaks corresponding to pyrrhotite. The pyrrhotite

peaks were relatively narrow, indicating that the particle size of the iron sulfide in the catalyst may be larger than desired for high catalyst activity. Sulfidation under these conditions may have mobilized the iron in the pillars so that some larger iron sulfide particle formed, as described by Lee and others (3). In contrast, the catalysts activated by in situ treatment with CS₂ did not show significant peaks for pyrrhotite or pyrite. Since sulfidation did occur, the iron sulfide species in these catalysts must be very minute. As described below, these catalysts had superior hydrocracking activities.

Surface areas of the fine particle and large particle iron-pillared clay catalysts were 156 and 181 m²/g, respectively. However, on sulfiding the fine particle iron-pillared clay catalyst in H₂S and H₂ at 400°C for 2 hours, the surface area dropped to 17 m²/g. The reduction in surface indicates an undesired collapse of the interlayer structure as the sulfide forms.

The hydrocracking activities of iron-pillared clay catalysts were determined by reactions with bibenzyl as the test compound. The reactions were carried out at 350°C for 3 hours in the presence of 1000 psi of molecular hydrogen in a 10-ml rocking autoclave reactor. Initially tests were conducted with 50 wt % catalyst in the bibenzyl, but later the tests used 10% catalyst concentrations. The catalysts were recovered in quantitative amounts, and no retrograde cationic condensation products or coke were observed during reactions.

A comparison of the bibenzyl hydrocracking results for the initial sulfided catalysts prepared from the fine and larger iron-pillared clay particles showed that the catalyst from the hematite-containing fines had a much lower activity (62% conversion) than the catalyst from the large particles (80% conversion). The lower activity of the catalyst from the fines was attributed to hydrolysis reactions that occurred prior to calcining. For the second batch of pillared clays that were rapidly collected, the bibenzyl hydrocracking activities of the sulfided catalysts were essentially identical for the fine and larger particles (79 and 80% conversion, respectively). This observation was consistent with the low hematite content of both precursors as demonstrated by the similar 2θ plots described above.

Examination of the products obtained from the reactions of bibenzyl with sulfided iron-pillared clays provided information on the nature of the hydrocracking activity for the catalysts. The major products were benzene, toluene, and ethylbenzene. Benzene and ethylbenzene were the largest products, and the amount of benzene was considerably more than ethylbenzene, indicating the further cracking of the ethylbenzene to benzene. These products are indicative of the Brönsted acid catalysis mechanism. The mechanism involves the ipso protonation of an aromatic ring of bibenzyl, followed by aryl-methylene bond cleavage to form benzene and phenylethyl carbonium ion. The phenylethyl carbonium ion is reduced to ethylbenzene by hydride transfer or hydrogenation, or it could undergo a variety of reactions to give other products. This reaction mechanism is common in reactions catalyzed by clays and clay-supported catalysts. The formation of toluene probably occurs via a Lewis acid catalyzed mechanism, since the temperature is too low for homolytic

cleavage of the central bond in bibenzyl. Reduction of carbonium ion intermediates in the reaction may or may not involve the iron sites.

The bibenzyl cracking products included many hundreds of other components, indicative of rearrangements and hydrogen addition as well as hydrocracking. Part of the single-ring aromatics was hydrogenated to give cycloalkanes in the reactions with sulfided catalysts. A substantial amount of methylcyclohexane was formed, probably from cleavage of the tertiary carbonium ion derived from phenylethylcyclohexane or hydrogenation of the ring-protonated bibenzyl. Minor components formed as a result of hydrocracking were propylbenzene, butylbenzene, tetralin, ethylbibenzyl, and phenylethylbibenzyl, etc. The alkylbenzene products resulted from hydrogenation of bibenzyl followed by cracking reactions, probably involving Lewis acid sites.

A second factor in determining the activity of the catalysts was the concentration of iron introduced into the clay. Use of a smaller amount of iron might result in a lower number of pillars and, consequently, result in a larger micropore volume. Exchange of one-third of the total equivalents of sodium by the triiron acetate cation rather than using an excess of the triiron gave a catalyst, after calcination and sulfidation of the large particle fraction, that was as active in hydrocracking reactions (79% conversion) as the catalyst prepared previously with excess triiron complex. The fine particle fraction had a lower activity (33% conversion).

The presence of excess sodium cations in the catalyst resulted in a serious loss of activity due association of the sodium with Brönsted acid sites in the clay or pillar. The sodium ions were exchanged out of one of the clays (from the fine particles) with ammonium ions following the iron-exchange. Calcination of this precursor to drive off ammonia gave a more active catalyst (64% conversion compared with 33%), because of regeneration of the Brönsted acid sites.

A comparison of the sulfided versus nonsulfided forms of the iron-pillared clays showed that the nonsulfided forms had a much lower hydrocracking activity (36 and 40% conversions for fine and large particles, respectively). These values are consistent with those obtained for other clay supports. Major products from nonsulfided catalysts were the same as those obtained with sulfided catalysts. The major difference in activity for the nonsulfided clays was the lower conversion, lower amounts of cyclohexanes, and lower proportion of ethylbenzene. Some of the reaction products were addition products of bibenzyl that may be regarded as Friedel Crafts addition products. However, extensive condensation and coke formation were not observed in the reaction. In comparison, acidic clay catalysts gave larger amounts of condensation products. Our results indicate that iron-pillared clays are effective in cleaving aryl-methylene and other C-C bonds at lower (350°C) temperatures.

In addition to catalysis of hydrocracking reactions at moderate temperatures, the iron-pillared clays were effective catalysts for catalyzing the hydrogenation of pyrene. Hydrogenation of pyrene with a sulfided ($\text{H}_2\text{S}/\text{H}_2$) iron-pillared clay catalyst at 350°C for 3

hr gave an 88% conversion to hydrogenated pyrenes at 50% catalyst concentration (Table 1). The hydropyrene yields were better than those obtained with sulfided nickel molybdenum under identical conditions (69%). Conversion to the hexahydropyrenes had not proceeded very far in the latter case.

3.2.2 Mixed Iron/Alumina-Pillared Montmorillonites

A general problem with the iron-pillared clays is that the calcination and/or sulfidation treatments appear to mobilize the iron and generate particles of the iron oxide and sulfide that are larger than desired for maximum utilization of the iron. Surface areas are substantially decreased, owing to collapse of the layer structure. The use of discrete mixed alumina/iron-pillared clays or of alumina-pillared clays as supports for pyrrhotite active sites may give a more effective particle size for the iron sites and more stable pillared structures. The aluminum pillars are stable to calcining and sulfidation treatments.

Alumina pillars were introduced by treatment of sodium montmorillonite dispersions with the oxyaluminum cation, and various methods were investigated for intercalation of the iron. Several pillared clay catalysts with discrete pillars composed of alumina and of iron oxide were prepared by intercalation of sodium montmorillonite first with oxyaluminum cations and then with oxyiron cations from ferric nitrate hydrolysis (sequential pillaring). These materials differed in the amounts of alumina and iron oxide introduced. After calcining and sulfiding with hydrogen sulfide/hydrogen mixture, these catalysts exhibited activities than the iron-pillared catalysts described above. At 50% catalyst concentrations, conversions of 85 to 88% were obtained in hydrocracking tests with bibenzyl. Neither the concentration of alumina or iron had a significant effect on the activities, and a relatively low iron concentration (500 ppm) was quite active in the tests.

A second method for preparation of the discrete pillars was utilized. In this method, the oxyaluminum cations and the oxyiron cations were added simultaneously to the sodium montmorillonite in large excess. The catalyst obtained by calcining and sulfiding as above was nearly equally effective (83% conversion) in hydrocracking tests with bibenzyl at 50% catalyst concentration. Thus, either the simultaneously or sequentially mixed pillared clays gave stable clays containing effective concentrations of iron sulfide and acidic sites for catalysis.

The third method for preparing mixed pillared clays utilized a mixed oxymetal cation complex composed mainly of aluminum with a small amount of iron. This alloy-pillaring gave a catalyst with lower activity in hydrocracking tests (72% conversion). X-ray diffraction showed that iron from the alloy pillar had been converted to pyrrhotite by the sulfidation; hence, the lower activity is probably due to some collapse of the pillared structure during this transformation of the iron.

Since the presence of sodium ions was found to exert a significant negative effect on hydrocracking conversion, one of the sequentially pillared catalysts was treated with ammonium nitrate in order to exchange out any remaining sodium ions. After calcination to volatilize the ammonia and sulfidation, the catalyst gave a slightly better conversion (89%) in the bibenzyl hydrocracking test at 50% catalyst concentration.

The method of sulfiding the iron in the mixed metal-pillared catalyst was also varied. By adding a small amount of carbon disulfide to the reaction rather than presulfiding the catalyst with hydrogen sulfide/hydrogen, a significantly higher conversion of bibenzyl was obtained (94%). The reason for higher activity is suspected to be that the pyrrhotite particle size is smaller with this method of sulfiding (see discussion above).

A mixed metal-pillared catalyst was tested with pyrene at 400°C in the rocking microreactor with 1000 psi of hydrogen (measured at room temperature). A 68% conversion of the pyrene was obtained (Table 1). Compared with the iron pillared catalyst discussed above, the lower yield for the iron/alumina-pillared catalyst at 400°C is consistent with the smaller equilibrium constant for hydrogenation at the higher temperature. Importantly, hydrocracking of the hydrogenated pyrenes was observed (36%) at 400°C. At 440°C, the conversion of pyrene dropped to 50%, and the yield of hydrocracked products increased (47%).

Table 1. Hydrogenation Activity of Iron Catalysts

H ₂ = 1000 psig, Sulfur = 0.03 g				
Catalyst (wt. %)	Substrate (mmol)	Temp. (oC)	Conv. (%)	Cracked Products (%)
None	Pyrene	400	6	0
IPC (50)	Pyrene	350	88	
IAPC (50)	Pyrene	400	67	36
IAPC (50)	Pyrene	440	50	47
Fe ₃ APC (10)	Pyrene	350	76	17
IMont (50)	Pyrene	400	68	25
NiMoCr PC (50)	Pyrene	400	64	36

Liquefaction testing with Wyodak subbituminous coal in tetralin solvent was performed with the discreet iron/alumina-pillared catalyst. The liquefaction reaction was carried out at 425°C for 1 hr in a 71-mL reactor with 1000 psi hydrogen (measured at ambient temperature). The catalyst was sulfided by adding a small amount of carbon disulfide. THF insolubles and pentane insolubles were measured by weighing. The pentane solubles contained the tetralin solvent; therefore, the oil yield was determined by the difference between the isolatable products described above and the maf coal weight (thus the amount includes gases and reaction product water). For this reaction, yields of THF solubles were 19%, toluene solubles were 25%, and oils/gases were 46%, with a total conversion to soluble products of 90%. These yield data are approximately the same as the thermal (no catalyst) data.

In an effort to improve the performance of the clay-supported iron catalyst, the preparation method was modified in several ways. One modification involved addition of the triiron complex to an alumina-pillared clay (4), rather than hydrolyzed ferric nitrate. The resulting discreetly pillared clay (Fe_3APC) exhibited very high activities in hydrocracking tests with bibenzyl at 10% catalyst concentrations (Table 2). Depending on the preparation

Table 2. Catalytic Hydrocracking of Bibenzyl

Reaction Temp. = 350°C, Reaction Time = 3 hrs, Sulfur = 0.10 g, H_2 = 1000 psig			
Catalyst (wt. %)	Conversion (%)	Benzene (mmol)	Ethylbenzene (mmol)
Fe_3APC (10)	84	1.79	0.57
Fe_3APC (10)	98	2.26	0.93
Fe_3ZPC (10)	67	1.28	0.34
K-10 Fe_3 (10)	65	1.38	0.40
IMont (10)	61	1.12	0.46
Magnetite (10)	3	Trace	
Maghemite (10)	5	Trace	
K-10 Fe_2O_3 (10)	57	2.40	0.26

methods, the bibenzyl conversions ranged from 84 to 98% and yields of benzene were high. Despite the high activity, not much condensation to higher molecular weight products occurred. Addition of triiron to the zirconia pillared clay gave a catalyst with lower activity in the bibenzyl cracking test. The Fe_3APC catalyst was also effective for pyrene hydrogenation and cracking (Table 1).

Liquefaction tests with the Fe_3APC catalyst (in situ sulfiding) were carried out with both as received (ARW) and acid-exchanged Wyodak (IEW) coal (Table 3). The conversion to THF solubles for the ARW was 91% with 53% heptane solubles. The conversion with the IEW was better (95%), but yields of heptane solubles were about the same (54%). Thus, the calcium in the low-rank coal did not contribute to extensive poisoning of the catalyst in this test. These data for the Fe_3APC catalyst may be compared with liquefaction data obtained in the same reactors and conditions but with a dispersed iron catalyst prepared by the PETC method. The reaction of ARW using the PETC iron impregnation method (5) gave 88% conversion to THF with 52% heptane solubles, whereas the IEW with the PETC method gave 91% conversion to THF soluble with 56% heptane solubles. Thus, the calcium poisoning appears to be significant for the dispersed iron catalyst.

For a reaction where the Fe_3APC catalyst was not sulfided, the conversion and heptane-soluble fraction dropped to 87% and 33% respectively. The reason why the conversion and yield drop below the thermal reaction values is that the highly acidic clay catalyzed retrogressive reactions. In contrast, when the highly dispersed iron sulfide is present on the clay, hydrogen is transferred to the cations generated on the clay acid sites, and reduction rather than condensation occurs.

The liquefaction of Blind Canyon coal was also investigated with the highly active Fe_3APC catalyst (Table 4). The conversion to THF solubles was 92% with 37% yield of heptane solubles. These data show a catalytic effect over the thermal reaction data, 91% conversion with 33% yield of heptane solubles.

To further evaluate the effectiveness of the mixed iron/alumina pillared clays for catalyzing hydrogenation and depolymerization reactions, conversion data for a solubilized coal intermediate was obtained and compared with that from other dispersed iron and molybdenum catalysts. Several reactions of a mineral-free low-severity intermediate from Wyodak coal (LSW) were carried out with the iron catalysts (Table 5). A THF-soluble intermediate was obtained by thermal liquefaction in tetralin solvent with $\text{CO}/\text{H}_2\text{S}$ and was separated from heptane-soluble products and solvent-derived materials by solvent (heptane) precipitation to give the high molecular weight LSW intermediate for these tests (6). The LSW is a low-density solid at ambient temperature, but melts easily. Since the substrate contains no heptane-soluble oils, the conversion of the asphaltenes to heptane-soluble oils can be readily determined in the product.

Table 3. Liquefaction Yields with Iron/Clay Catalysts

Reaction Temp. = 425°C, Reaction Time = 1 hr, H ₂ = 1000 psi (cold) Coal/tetralin = 0.5, Catalysts = 10 wt%					
Coal (g)	Catalyst (wt. %)	Sulfur (g)	Conv. (%)	Heptane-I (%)	Heptane-S (%)
ARW (7.0)	None	None	89	41	48
IEW (5.3)	None	None	86	40	47
ARW (7.0)	Fe ₃ APC (10)	None	87	54	33
ARW (7.0)	Fe ₃ APC (10)	0.10	91	38	53
IEW (5.34)	Fe ₃ APC (10)	0.10	95	41	54
IEW (5.41)	K10Fe ₃ (10)	0.10	92	35	57
ARW (7.0)	IMont (10)	0.10	93	26	67
IEW (5.37)	IMont (10)	0.10	95	26	69

ARW = as received Wyodak

IEW = 7.0 g AR coal was acid-washed and dried

A thermal (noncatalytic) reaction of the LSW in tetralin at 425 °C for 1 hr in 1000 psi hydrogen gave 15% conversion to heptane-solubles (Table 5). The 15% value for the LSW substrate represents a conversion of preasphaltenes and asphaltenes to mainly heptane-soluble oils and a small amount of water, but essentially no formation of carbon dioxide and hydrocarbon gases. A small amount of hydrogen transfer from the tetralin solvent is believed to occur and is accompanied by some dehydration to give a somewhat more soluble product.

Table 4. Catalytic Liquefaction with Blind Canyon Coal

Reaction Temp. = 425°C, Reaction Time = 1 hr, H ₂ = 1000 psi (cold) Coal/tetralin = 0.5, Catalysts = 10 wt%				
Catalyst (wt. %)	Sulfur (g)	Conv. (%)	Heptane-I (%)	Heptane-S (%)
None	None	91	58	33
Fe ₃ APC (10)	None	93	61	32
Fe ₃ APC (10)	0.10	92	55	37

The liquefaction reaction of the LSW in tetralin with the mixed iron/alumina-pillared clay catalyst (in situ sulfided) gave 30% conversion to heptane-solubles under the same conditions. The weight of catalyst used corresponded to 10% of the weight of low-severity intermediate; the iron content used in the reaction was thus 1% of the intermediate. This ratio is the same as that used in reactions with the coals. Since the catalyst can be easily recovered from the second stage reaction, it might be used in much greater amounts in an actual process; however, the ratio was kept low in these experiments to provide more discriminating data for catalyst evaluation.

The two-fold increase in conversion to oils for catalytic versus thermal reactions with the LSW substrate can be attributed to both hydrocracking and hydrogen transfer reactions catalyzed by the sulfided iron on the highly acidic pillared clay support. Depolymerization of the coal is impossible to measure directly for small amounts of substrate in a donor solvent, because of inaccuracies in both distillation and GC methods.

Table 5. Catalytic Liquefaction of LSW Intermediate

Temperature = 425°C, H ₂ = 1000 psi, LSW/Tetralin = 0.5, S = 0.01g				
Catalyst (wt. %)	Time (hr)	THF-I	Heptane-I	Heptane-S
None	1	0	85	15
Fe ₃ -APC (10)	1	0	70	30
Fe ₃ -APC (10)	3	0	58	42
IMont (10)	1	0	55	45
Co-Moly (10)	1	0	49	51

3.2.3 Iron-Impregnated Montmorillonite

Because the combinations of sulfided iron with pillared clay exhibited good hydrocracking and hydrogenation catalysis with model compounds, but were only moderately successful with Wyodak coal, an alternative method for dispersing iron on a clay surface was investigated. Addition of either triiron complex or ferric nitrate to an acid-washed montmorillonite followed by hydrolysis by ammonia addition gave the iron hydroxyoxide-impregnated clay precursor (4). More of the iron should be on the surface faces and edges of the clay and less in the interfacial volumes than was the case for the pillared clays.

The activities of the iron-impregnated montmorillonites were tested with bibenzyl (in situ sulfidation) (Table 2). The Fe₃-impregnated K-10 montmorillonite (Fe₃K10) gave a higher conversion (65%) than the ferric-impregnated K-10 montmorillonite (IMont). These conversions were lower than those obtained with the mixed iron/alumina pillared clays. This difference could be attributed to the higher acidity of the pillared clay support. Hydrogenation activity was tested with pyrene at 400°C (in situ sulfidation). The IMont catalyst gave a good conversion to hydropyrenes and a somewhat lower amount of cracked products, compared with the mixed iron/alumina pillared montmorillonites (Table 1). Again this difference in activity can be attributed to the higher acidity of the pillared clay supports.

Liquefaction of Wyodak coal with the iron-impregnated clays gave high conversions to THF solubles as well as heptane solubles. Initial tests with IMont catalyst with as received Wyodak coal (1 hr, 425°C) gave 93% conversion to THF solubles and 67% conversion to pentane solubles (Table 3). The test was repeated with another batch of IMont which resulted in the same conversion 93% to THF solubles and 67% to heptane solubles.

Liquefaction of an acid-exchanged Wyodak sample gave 95% conversion to THF solubles and 69% to heptane solubles. The Fe₃K10 gave 92% conversion to THF solubles and 57% to heptane solubles.

Since the hydrocracking activity for the IMont reaction with bibenzyl is lower than that of the mixed iron/alumina-pillared montmorillonite catalyst, the higher activity of the IMont with the initial Wyodak coal (both as-received and acid exchanged) and also with LSW (see below) can be attributed to a higher effective iron concentration on the surfaces available to the coal-derived macromolecules. Much of the iron intercalated into the pillared clay may not actually be accessible after sulfidation or at the reaction is diffusion limited. Some preliminary studies were needed to determine the optimum concentration of iron supported on the K-10 montmorillonite.

In order to determine the effect of iron concentration on the liquefaction yields of coals, three catalysts with different concentration of iron hydroxy oxide (2.5, 5 and 10 wt%) supported on acid treated montmorillonite (K-10) were prepared simultaneously by ammoniation of the ferric nitrate- impregnated K-10 montmorillonites and were tested for the liquefaction of wyodak subbituminous coal. The liquefaction reactions were carried out by heating a well stirred slurry of 7 g as-received coal, 10 wt% catalyst, 2 wt% sulfur for in situ sulfidation of the catalyst and 14 g tetralin (solvent) in 1000 psi of initial hydrogen at 425°C for 1 hour (Table 6). The uncatalyzed (thermal) reaction of ARW coal gave 89% conversion of coal to THF-soluble products, with 48% being heptane-soluble products. The reaction with catalyst containing 5 wt% iron gave 97% conversion to THF-soluble products, with 57% being heptane-insoluble (oils). Compared with the catalyst containing 2.5 wt% Fe, this catalyst gave slightly higher overall conversion and conversion to oils. The reaction with catalyst containing 10 wt% Fe also gave a slightly lower conversion to THF-soluble (96%) as well as heptane-solubles (55%) than the catalyst containing 5 wt% Fe. These results seems to indicate that the low concentration of iron is enough to effect the hydrogenation of intermediates produced during liquefaction, and additional iron may just make the iron cluster size larger without increasing its effectiveness.

Previous results showed (7) that K-10 montmorillonite-supported iron hydroxyoxide with 2.7 wt% Fe (IMont) gave significantly better conversions of coal to THF-soluble (93%) and heptane-soluble (67%) products than the catalysts used in this comparison. This could be attributed to variations in the preparation, such as the rapidity of the drying, or perhaps to some other unknown effect. Rapid drying was demonstrated to be extremely important in determining the activity of the iron/clay catalysts in tests with bibenzyl.

The effect of reaction time was determined by conducting the liquefaction reaction of Wyodak coal with K-10/FeOOH (2.5 wt% Fe) for 3 hours period. Compared with one hour reaction, three hours reaction gave the same conversion (95%) to THF-soluble products and higher conversion to heptane-soluble products.

Liquefaction testing was also performed with these catalysts to determine the depolymerization activity with the Wyodak low-severity intermediate. The IMont catalyst gave 45% conversion of the LSW asphaltenes to heptane-soluble oils in a 3 hr test (Table 5). The thermal reaction of the LSW at 425°C for 3 hrs gave 31% conversion to heptane-soluble oils. As in the tests with as received and acid-exchanged Wyodak liquefaction discussed above, the activity of the IMont in the LSW liquefaction tests is substantially higher than that of the mixed iron/alumina pillared catalyst. The activity of the IMont is a little lower than that of commercial cobalt/molybdenum catalyst with the LSW (51% conversion to heptane solubles).

To determine the effects of longer reaction time periods on the conversion yields, the heptane-insoluble material left at the end of the catalytic liquefaction was further reacted with fresh catalyst. This reaction gave 30% conversion of the heptane-I material to heptane-soluble products (oils). This additional conversion of the heptane-insoluble material suggests that the depolymerization reaction continues to progress with the iron/clay catalysts at a modest rate under these conditions.

Table 6 Catalytic Liquefaction of Wyodak Coal

Coal (as-received) = 7.0 g, Tetralin = 14 g, Sulfur = 2 wt%, H ₂ = 1000 psi, Reac. Temp. = 425°C				
Catalyst (wt. %)	Reac. Time (hrs)	Conversion (%)	Heptane-I (%)	Heptane-S (%)
None	1	89	41	48
K-10/FeOOH* (10)	1	95	41	54
K-10/FeOOH* (10)	3	95	37	58
K-10/FeOOH** (10)	1	97	40	57
K-10/FeOOH*** (10)	1	96	41	55

* = Catalyst contains 2.5 wt. % iron.

** = Catalyst contains 5 wt iron.

*** = Catalyst contains 10 wt% iron.

The success with montmorillonite-supported iron hydroxyoxide brings to question a comparison with iron hydroxyoxide on other acidic supports, such as zeolites or an alumina-silica support. This idea was tested by preparing supported iron hydroxyoxide by the ammoniation reaction of ferric nitrate impregnated on a commercial FCC catalyst consisting of a zeolite/aluminosilicate cogel. The reaction of bibenzyl with the FCC cracking catalyst itself gave 40% conversion to lighter products. Major products were benzene (0.95) and ethylbenzene (0.36) along with a small amount of toluene (0.12). A similar reaction with FCC-supported iron hydroxyoxide gave significantly higher conversion (48%) of bibenzyl to benzene, toluene and ethylbenzene (table-1). Another FCC-supported iron hydroxyoxide prepared by a modified procedure (ion exchange rather than incipient wetness impregnation) gave a slight improvement in the hydrocracking of bibenzyl. Product distribution was the same as before. Comparison of these results with those obtained with clay-supported iron catalysts showed that they were far inferior, and no further testing was done with these catalysts.

Table 7 Catalytic Hydrotreating With FCC-Supported Catalysts

Reaction Temp. = 350°C, Reaction Time = 3 hours Sulfur = 2 wt%, H ₂ = 1000 psig			
Catalyst (wt%)	Substrate (mmol)	Conv. (%)	Major Products (mmol)
FCC (10)	Bibenzyl (2.75)	40	Benzene (0.95) Toluene (0.12) Ethylbenzene (0.36)
FCC/FeOOH-1 (10)	Bibenzyl (2.75)	48	Benzene (1.20) Toluene (0.20) Ethylbenzene (0.41)
FCC/FeOOH-2 (10)	Bibenzyl (2.75)	50	Benzene (1.21) Toluene (0.15) Ethylbenzene (0.50)

3.2.4 Iron Oxoaluminate-Impregnated Montmorillonite

One of the major goals in coal liquefaction is prevention of agglomeration and sintering of the fine catalyst particles or clusters. A new route to the formation of catalysts has been explored by the use of oxymetallate groups attached to the transition metal precursor. The oxymetallate groups are intended to form a stabilizing matrix around the transition metal site in the active catalyst. Early studies of these catalysts have been directed to both fundamental questions of reactivity and mechanism as well as direct coal liquefaction.

Iron oxotitanate hexaisopropoxide and iron oxoaluminate tetraisopropoxide were generated by heating titanium isopropoxide or aluminum isopropoxide and ferrous acetate in tetralin in a stream of dry nitrogen. Distillation of isopropyl acetate formed during reaction gave a green solution of iron oxoaluminate in tetralin (8). Iron oxotitanate was a reddish solution in tetralin. Iron oxoaluminate and iron oxotitanate showed considerable hydrogenation and liquefaction activity for pyrene and Wyodak coal respectively (9). In an attempt to boost the hydrocracking activity of iron oxometallates, iron oxoaluminate and iron oxotitanate were supported on an acidic support (acid-treated montmorillonite, K-10).

Iron oxotitanate supported on acid-treated montmorillonite (K-10) was tested for the hydrotreating of bibenzyl and pyrene (Table 8). Reaction of bibenzyl with 10 wt% of the catalyst gave 55% conversion of the bibenzyl to lighter products. Major products were benzene (1.35 mmol) and ethylbenzene (0.65 mmol) along with small amount of toluene (0.16). Reaction of this catalyst with pyrene gave high conversion (71%) of the substrate to hydropyrenes. Major products were di-, tetra- and hexahydropyrene along with small amounts of decahydropyrenes (3-isomers). No coke or oligomeric products were formed indicating the absence of retrograde condensation reaction. Compared with K-10-supported iron oxoaluminate, K-10-supported iron oxotitanate exhibits higher hydrogenation and hydrocracking activities (9).

To test the liquefaction/depolymerizing activity of the sulfided catalysts formed from these soluble precursors, Wyodak subbituminous coal was catalytically treated as described above. The reaction was carried out by heating 7 g of the coal and 14 g tetralin with 10 wt% of the catalyst precursor and 2 wt% of elemental sulfur (for in situ sulfidation) at 425°C for 3 hours in 1000 psi of initial hydrogen pressure. The conversion data are given in Table 9.

The reaction of Wyodak with sulfided iron oxoaluminate catalyst gave a high conversion (94%) of the coal into THF-soluble products, 54% being heptane-soluble oils. Similar reaction using iron oxoaluminate supported on K-10 gave almost identical conversions (Table 9). K-10-supported iron oxotitanate gave higher conversions than iron oxoaluminate-supported catalyst. However, the conversion to heptane-soluble oils obtained with supported iron oxotitanate were significantly higher than that obtained with iron oxoaluminate. Although these catalysts are not more successful than the clay-supported iron (IMont), they demonstrate that surrounding the iron (sulfide) with a matrix of alumina or titania decrease the activity by a small factor. This answers a question we raised about the effects of oxymetallates that are present in mixed iron/alumina-pillared clay catalysts. We conclude that a somewhat higher liquefaction activity occurs in a catalyst where the iron sulfide is proximate to the clay layer.

Table 8. Hydrogenation Activity of Iron Oxometallates

Temperature = 400°C, Time = 2 hrs, H ₂ = 1000 psig, S = 0.03 g		
Catalyst (wt. %)	Substrate (mmol)	Conv. (%)
None	Pyrene	6
IOAl (10)	Pyrene	67
IOAl-recovered (10)	Pyrene	66
IOAl/K10 (10)	Pyrene	71
IOTi (10)	Pyrene	80
IOTi/K10	Pyrene	71
CoOAl (10)	Pyrene	67
None	1-MeNaphthalene	2
IOAl (10)	1-MeNaphthalene	77

IOAl = Iron oxoaluminate solution in tetralin.

IOIi = Iron oxotitanate solution in tetralin

IOAl/K10 = IOAl impregnated on K-10

Table 9. Catalytic Reactions of Iron Oxometallates

Reaction Temp. = 425°C, Time = 1 hr, H ₂ = 1000 psi, Coal wt./Tetralin = 0.5				
Coal	Catalyst (wt %)	Fe conc (ppm)	Conv. (%)	Heptane-S (%)
Wyodak	IOAl (2.5)	5600	94	54
Wyodak	IOAl (25)	56000	94	60
Blind Canyon	IOAl (25)	56000	91	51
Wyodak	IOAl/K10 (10)	6520	96	52
Wyodak	IOTi	56000	97	67
Wyodak	IOTi/K10 (10)	5800	98	59

3.2.5 Mossbauer Characterization Results on Clay-Supported Iron Sulfide Catalysts

Mossbauer spectra were obtained for two of the sulfided catalysts prepared from iron-impregnated montmorillonites. Spectra were recorded at three temperatures (293 K, 77 K, and 4.5 K) in order to determine the effects of superparamagnetic relaxation.

The highly active catalyst prepared by addition of ferric nitrate to montmorillonite followed by ammonia treatment was sulfided with sulfur under hydrogen pressure. The spectrum of this sample at 293°K exhibited only a three peak spectrum composed of two doublets. These lines are attributed to an iron sulfide phase (IS = 0.28, QS = 0.86; 68%) and a high spin Fe⁺² component (IS = 1.14, QS = 2.58; 32%). The high-spin Fe⁺² was attributed to an oxidic phase similar to that found by Ramselaar on supported catalysts (10). None of the 6-line pyrrhotite pattern was present. The spectrum at 77 K was similar, indicating that the domain size of the iron sulfide sites is very small.

The spectrum of this sample at 4.5 K clearly exhibited relatively intense hyperfine split peaks (6-line pattern) in addition to the high spin Fe⁺² doublet component. From the very large magnitude of the hyperfine splitting (hyperfine field = 46 T), the composition of the iron sulfide can be determined. Only greigite (Fe₃S₄) has a internal field this large (11). By contrast, the hyperfine fields in pyrrhotite and other Fe_{1-x}S minerals are less than 31 T.

The temperature behavior of the spectra of this sample is consistent with a very small particle domain size for the greigite phase. The effects of domain size on superparamagnetic relaxation have been systematically examined for iron oxides, but not for iron sulfides. Thus,

particle size distributions cannot be determined for the supported iron sulfide catalysts, but since the hyperfine interactions are only observed at 4.5K, the particle size must be very small.

The 293 K spectrum of the sample prepared by impregnation of triiron acetato complex and subsequent sulfidation was similar to that of the sample described above. Two components corresponding to an iron sulfide (72%) and a high spin Fe^{+2} (28%) were found. Some slowly relaxing background phase is evident for this sample, suggesting a larger domain size for this system. The 77 K spectrum exhibits some additional complexity compared with the 293 K spectrum of this sample and with the other sample. The major peaks are again the high spin Fe^{+2} doublet and the iron sulfide doublet ($\text{IS} = 0.30$, $\text{QS} = 0.71$), but the 77K spectrum of this sample exhibited a number of smaller peaks composing several 6-line systems. The appearance of these peaks in the lower temperature spectrum can be attributed to the larger particle size distribution of iron sites in this sample. At the higher temperature, the superparamagnetic relaxation effect collapses these hyperfine peaks in the larger domains in this sample. The 6-line component systems were impossible to resolve and may represent more than one iron sulfide phase.

This sample also exhibits a complex spectrum at 4.5 K. Besides the high spin Fe^{+2} doublet, intense peaks for hyperfine systems are present. The major component (greigite) has a similar very large hyperfine splitting (hyperfine field = 47 Tesla).

To summarize the Mossbauer data, sulfidation of clay-supported iron oxides gave an iron sulfide phase with low isomer shift. The large hyperfine splitting observed in the 4.5 K spectrum is consistent with the greigite composition. A high spin Fe^{+2} doublet was observed that could be attributed to diffusion of iron into the clay support. Since greigite and a high spin Fe^{+2} (oxidic) phase are the major components present in both catalysts, the form of the iron cation (Fe^{+3} versus Fe_3 complex) used in the preparation does not appear to be a major factor in determining the form of iron sulfide sites on the clay support. On the other hand, the clay support had a major influence and may have significantly interacted with the iron during or prior to the formation of the sulfide. Ramselaar and others have already shown that significant differences in iron sulfide composition are found for carbon-supported, alumina-supported, and unsupported iron sulfides. Low temperature spectra are needed to further characterize those compositions. The clay-supported catalysts represent another composition. Further studies on the effects of supports, solvents, hydrogen pressure, etc. would greatly benefit our understanding of how to maximize the activity of iron sulfide catalysts.

4.0 SUMMARY AND CONCLUSIONS

A. Iron-pillared clay catalysts.

- 1. Catalysts prepared by exchange of triiron clusters on montmorillonite and in situ sulfidation gave catalysts with high hydrocracking activity.**
- 2. Hydrocracking activity in iron-pillared clays was highest when prepared by rapid collection and rapid drying of particles and ammonia treatment.**
- 3. Hydrocracking activity is related to Bronsted sites on the clay as well as maghemite content of intermediate oxide.**
- 4. Iron-pillared clays are effective catalysts for hydrogenation and prevent the acid-catalyzed retrogressive condensation reactions that occur with clays.**

B. Mixed iron/alumina-pillared clay catalysts.

- 1. Several methods for preparing mixed iron/alumina pillared montmorillonites gave highly active catalysts.**
- 2. Mixed pillared clays had more stable surface areas following sulfidation than iron-pillared clays.**
- 3. Hydrogenation and hydrocracking of pyrene was comparable to that observed with zeolites and zinc chloride.**
- 4. Liquefaction with Wyodak coal gave improved conversions to heptane solubles (53%) compared with thermal (48%).**
- 5. Use of acid-exchanged Wyodak showed a small improvement in conversions.**
- 6. Liquefaction of Blind Canyon coal gave 37% conversion to heptane-solubles, compared with 33% for thermal reaction.**
- 7. Catalytic hydrogenation of a Wyodak low-severity product (3 hr) gave 47% conversion of asphaltenes to heptane solubles, compared with 26% thermal and 67% with Co-Moly catalyst.**

C. Iron-impregnated clay catalysts.

- 1. Iron hydroxyoxide-impregnated montmorillonites were prepared which gave highly active catalysts for hydrocracking, hydrogenation, and coal liquefaction after sulfidation.**
- 2. Liquefaction with Wyodak coal gave high conversion to heptane solubles (67%) similar to Co-Moly catalyst.**
- 3. Acid-exchanged Wyodak gave improved conversion to heptane solubles (69%).**
- 4. Catalytic hydrogenation of low-severity Wyodak product (1 hr) gave 45% conversion of asphaltenes to heptane solubles, compared to 51% with Co-Moly.**

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