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FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

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by

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DISCLAIMER

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1.0 EXECUTIVE SUMMARY

The investigation of methods for the production and testing of iron-pillared clay catalysts was continued in this quarter. The surface area of the mixed alumina/iron pillared clay catalyst decreased to 51 m^2/g on sulfidation. Thus the stability of the alumina pillars during the sulfidation and thermal treatments prevented the total collapse that occurred in the case of the iron-pillared clays.

Previously the mixed alumina/iron pillared clays were tested for hydrocracking activities with bibenzyl. This testing was extended to a determination of activity with a second model compound substrate (pyrene), representative of the polynuclear aromatic systems present in coal. The mixed alumina/iron-pillared catalysts were effective in both hydrogenating and hydrocracking pyrene at 400 and 440°C. Results that were almost identical to those obtained with a sulfided pillared clay-supported Ni-Mo catalyst were obtained. Since pyrene hydrocracking is usually only observed with catalysts with high acidities, such as zeolites and zinc chloride, this result demonstrates a high potential for the clay-supported iron sulfide catalysts in coal liquefaction. Despite the high acidity, no coking was observed, as one might expect from a zeolite catalyst. This is attributed to the synergistic effect that results from hydrogen activation by the iron sulfide in the vicinity of the acid sites, such that hydrogen or hydride transfer to cationic intermediates is facilitated and their transformation to high molecular weight products is avoided.

Testing of the mixed alumina/iron-pillared catalysts with 1-methylnaphthalene gave interesting results that demonstrate shape selectivity. These studies compared the mixed pillared clay catalysts with the iron impregnated clay catalysts with respect to the ratio of 1- to 2-methylnaphthalene and 1- to 2-methyltetralin obtained. Both of these ratios were considerably lower for the mixed pillared clay catalyst. This might be expected on the basis that the width of the 2-methylnaphthalene is lower and may be a preferred product in the interstitial spaces of the pillared clay catalyst.

The clay-supported iron hydroxyoxide catalysts prepared by impregnation of iron species on acidic clays were further investigated. Sulfidation of these catalysts using the carbon disulfide in situ method gave hydrocracking activities with bibenzyl that were somewhat less than those obtained by presulfidation with H_2/H_2S mixtures. Further work is required to understand the types of iron oxide and sulfide structures that are involved and the relationship to the reactivity.

Liquefaction of Wyodak subbituminous coal was very successful with the iron impregnated clay catalyst, giving a highly soluble product. High conversions were also obtained with the mixed alumina/iron-pillared clay catalyst, but the yield of oil-solubles was considerably lower.

Several new catalysts were synthesized with the idea of decreasing the pillar density and thereby increasing the micropore volume. These catalysts were prepared by first pillaring with an organic ammonium pillaring agent, then introducing a lower number of silica or alumina pillars. Finally the iron component was added either before or after thermal removal of organic pillars.

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 proposed research is 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 constitute the active catalytic sites for hydrogenation of the coal and the solvent used in the liquefaction. The pillaring catalytic sites are composed of pyrrhotite, which has been previously demonstrated to be active for coal liquefaction. The pyrrhotite 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 proposed work will evaluate methods for preparing the fine particle iron-pillared clay dispersions and for activating the particles to generate the catalysts. Characterization studies of the pillared clays and activated catalysts will be performed. The effectiveness of the pillared clay dispersion for hydrogenation and coal liquefaction will be 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 continued. These catalysts consist of sulfided iron clusters 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 controlled and made larger than those of the zeolites, and hence are more suitable for the adsorption the 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.

Work in the fourth quarter continued the study of preparation methods for iron-pillared montmorillonites. The sodium form of this clay 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 will be determined in subsequent studies.

3.2 Experimental

3.2.1 Catalyst Preparation

3.2.1.1 Preparation of Trinuclear acetato-hydroxo iron (III) nitrate

Trinuclear acetato-hydroxo iron(III) nitrate, $[Fe_3(OCOCH_3)_7OH.2H_2O]NO_3$ was prepared according to the method reported by Yamanaka et al. (3). Detailed procedure has been described in the previous quarterly report (2).

3.2.1.2 Preparation of Pillared Clay Catalysts

Preparation of mixed alumina-iron Pillared clay catalyst (DS-.21A.67IPC) has been described previously (4).

Dodecylammonium montmorillonite was prepared by adding dodecylamine (8.82 g) to 4.8 mL of conc. HCl in 100 mL of water in a 1 L round bottom flask and heating to 80°C with stirring. To the dodecylammonium solution was added a suspension of 20 g of sodium montmorillonite in 400 mL of water which had been preheated to 80°C. Stirring was continued at 80°C for 1 hr. The thick slurry was centrifuged at 3500 rpm for 2 hr. The residue was reslurried with 400 mL of hot water, stirred for 1 hr, and centrifuged. The hot water washing was repeated a second time. The residue was vacuum-dried at 100°C to give 22.2 g of grey solid.

The mixed silica/dodecylammonium-pillared montmorillonite was prepared by stirring 5.55 g of the dodecylammonium montmorillonite with 33.2 g of tetraethyl orthosilicate for 48 hrs. The product was suction-filtered. This mixed pillared clay was heated at 538°C to decompose and volatilize the dodecylammonium pillars. A tan powder was obtained (3.82 g). An aqueous ferric nitrate solution (0.1 g in 10 mL water) was added to 0.5 g of the calcined silica-pillared montmorillonite slurried in 25 mL of water. the ferric ion was taken up by the clay structure to give a tan suspension that was stirred for 1 hr. The iron-impregnated silica-pillared montmorillonite was dried at 538°C to give 0.48 g of rusty tan granules. Similar procedures were used for other organic-inorganic pillared catalysts.

3.2.1.3 Preparation of Supported Clay Catalysts

Acid treated montmorillonite K-10 (surface area 220-270 m^2/g) obtained from Aldrich Chemical company was used without further purification. Iron hydroxy oxide was supported on acid treated montmorillonite K-10 according to the method of Cugini and co-workers (5). The detailed procedure has been described in our previous report (4). Triiron was also supported on acid washed montmorillonite K-10 using previously described procedure (4).

3.2.1.4 Sulfidation of Catalysts

The desired catalyst (ca. 1 g), solvent (decalin, 8 g), and small amount of carbon disulfide (0.1 g) were placed in a 70 ml Parr reactor. The reactor was evacuated, pressurized with 1000 psi of H_2, and placed in a rocking heater preheated to 350°C. The heating was continued for 2 hours. The reactor was then cooled to room temperature, degassed, and the sulfided catalyst was separated by centrifugation and washing with dichloromethane. The sulfided catalysts were dried in vacuo and stored in air tight ampules.

For the reactions involving in situ sulfidation of the catalyst, small amount of carbon disulfide was added along with the catalyst.

3.2.2 Analytical procedures and Instrumentation

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped a Petrocol capillary column. A mixture of 2,2,4-trimethylpentane and n-octadecane was the internal standard. GC/FTIR/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron film of DB-5.

For X-ray powder diffraction (XRD) analysis, the pillared clay is ground with water and smeared onto a single crystal, "zero"-background, quartz plate to obtain oriented specimens that give intense 001 basal reflections. Diffraction data are collected in 0.02° steps for one second dwell time using a Philips automated diffractometer equipped with a copper tube, theta-compensating slit, graphite diffracted beam monochromator, and scintillation detector. Software programs supplied by Materials Data Incorporated are used for data collection, data reduction, and phase identification.

Surface area measurements were performed with Micromeritics Accu Sorb 2100E static unit for nitrogen physisorption at 77K (BET method).

3.2.3 Catalytic hydrotreating of Model Compounds

In a typical run, 0.50 g of the test compound, 0.25 g of the desired catalyst and 0.04 g of the carbon disulfide (only for in-situ sulfidation of catalyst) were placed in a microreactor (tubing bomb). The microreator was evacuated and pressurized with 1000 psi of hydrogen, and placed in a rocking autoclave heated to 350°C for 3 hours. At the end of the reaction period, The microreactor was cooled to room temperature, degassed, and opened. The desired amount of the internal standard was added to the product slurry, and the product slurry was transferred into a centrifugation tube by washing with methylene chloride, and solid catalyst removed by centrifugation. The liquid sample was analyzed by GC-FID and GC/FTIR/MS. The solid was dried in vacuum at 110°C for 3 hours.

3.2.4 Liquefaction of Coal

A slurry consisting of 7.0 of coal (as received Wyodak-Clovis Point, 71.% maf, 22.1 moisture, and 6.6% ash), 0.70 g of desired catalyst, small amount of carbon disulfide (0.1 g) for in-situ sulfidation of catalyst, and 14 g of solvent (tetralin) were placed in a 70-ml Parr reactor. The reactor was evacuated and charged with 1000 psi initial pressure of H_2. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for one hour. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed.

The product slurry was extracted with pentane, toluene, and tetrahydrofuran (THF). The pentane soluble fraction was mixed with appropriate internal standard and analyzed by high resolution GC. The toluene-soluble, THF-soluble, and THF-insoluble fractions were dried in vacuo at 110°C and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The conversion and yield data are given in Table 4.

3.3 Results and Discussion

3.3.1 Preparation of New Catalysts: Synthesis of pillared montmorillonites with large pore volumes.

One of the main advantages of pillared clay supports is the potentially large surface areas available between the clay layers for anchoring the active metal sites. To achieve these large areas on the clay support, the pillar density must be small so that the interstitial space is not crowded with pillars. Several methods for limiting the pillar density have been attempted. These include using lower concentrations of the pillaring cations (5), introduction of competing cations (5), and building on an organic pillar framework (6). In the work with the mixed aluminum/iron pillared clays, some low concentrations of aluminum and iron oxycations were used, but the effects on the conversions were insignificant in the different compositions. An alternative that was previously used by Landis and others (6) for preparation of layered titanates with a low density of alumina pillars was adapted for use with the montmorillonites. In this preparation, an organic pillaring reagent (dodecylammonium ions) is introduced to preswell the layered structure, and the inorganic pillaring precursor reagent was then absorbed into the interlayer space. The precursor is tetraethyl orthosilicate (TEOS) or another one of the typical alkyl metalates commonly used in the preparation of ceramics, zeolites, or synthetic clays. The organic pillaring reagent is decomposed and driven out by calcining. Iron was intercalated or impregnated into the pillared clay at various stages of the preparation.

Specifically, the following large pore montmorillonite catalysts were prepared in this quarter:

1. Iron-impregnated (2.6%) silica-pillared montmorillonite by reaction of TEOS (neat) with dodecylammonium montmorillonite (DDAM), followed by calcination to remove organic pillars and impregnation of iron nitrate solution. Final calcination gave a tan material.

2. Iron-impregnated (2.6%) silica-pillared montmorillonite by reaction of TEOS in dimethylformamide (DMF) solution with dodecylammonium montmorillonite (DDAM). The reaction produced a gel in the DMF, only part of which could be separated from the solvent by centrifugation. The DMF and excess TEOS were removed from the supernatant by addition of water and further centrifugation. The resulting mixed DDA/silica-pillared montmorillonite was dried and calcined to remove the organic pillars. Ferric nitrate was then impregnated into the silica-pillared clay and the calcination gave a tan material.

3. Triiron-intercalated silica-pillared montmorillonite by reaction of TEOS with DDAM in DMF as above, and then intercalating triironheptaacetato complex prior to calcination. The material produced from this reaction was black and very light. It appeared that the decomposition of the DDA pillars formed a lot of carbon dispersed in the clay structure.

4. Triiron-pillared montmorillonite by reaction of triiron complex with DDAM in aqueous conditions. Calcination of this product also produced a black material.

5. Triiron-pillared montmorillonite by reaction of triiron complex with DDAM in DMF. Again, a black material was obtained.

6. Iron-impregnated alumina-pillared montmorillonite by reaction of aluminum isopropoxide with DDAM in methanol to give the mixed alumina/DDA-pillared montmorillonite, followed by calcination and impregnation of aqueous ferric nitrate. The product was tan.

7. Triiron-intercalated alumina-pillared montmorillonite by isolating the mixed alumina/DDA-pillared montmorillonite as described above from the reaction of aluminum isopropoxide with DDAM in methanol, followed by addition of triiron complex and calcination. As with the other catalysts where triiron was added prior to calcination, the product was black.

In general, the treatments of the DDA with various pillaring reagents gave material with very low densities. We presume that will have correspondingly high surface areas and large micropore volumes. Testing of the catalysts for hydrocracking is currently under investigation. The carbon-containing clays may have interesting absorptive properties in addition to any catalytic activity.

Future work will involve using another alternative for low-density pillars. This technique will use polyvinyl alcohol (PVA) as an additive during pillaring with alumina and iron. By complexing the intercalated cations in the interstitial space, a greater pore volume can be obtained in catalyst after calcination to remove the PVA.

3.3.2 Characterization of Catalysts

Previous results have shown that iron oxide pillars do not survive sulfidation, and layer structure of the clay collapses upon sulfidation resulting in very low surface area solids (2). Stable discrete alumina-iron pillared clays were prepared by sequential intercalation of montmorillonite with polyoxy aluminum (Al_{13}) and polyoxy iron (Fe_3) cations. The surface area of the mixed pillared clay catalyst (DS.21A.67IPC) was 120 m^2/g. This catalyst was sulfided by heating in decalin with small amount of carbon disulfide at 350°C for 2 hours in the presence of 1000 psi of initial H_2 pressure. The surface area of the sulfided catalyst was significantly lower (51 m^2/g) than the non-sulfided catalyst. However, the decrease in surface area is significantly smaller than iron-pillared clay reported earlier (2). This is due to the presence of stable alumina pillars which unlike iron pillars do not collapse during sulfidation and thus maintain the layered structure of the clay. The reduction in surface area is attributed to the loss of iron pillars and pore plugging by the iron sulfide formed as a result of sulfidation.

Methods for conversion of the oxyiron-intercalated clays to active sulfide forms were compared. The mixed aluminum-iron (DS-.21A.67IPC) pillared montmorillonite and iron hydroxyoxide supported K-10 were sulfided by heating with carbon disulfide in decalin at 350°C for 2 hours in the presence of 1000 psi of initial hydrogen pressure. The sulfided catalysts were characterized by X-ray diffraction (XRD) analysis, and results compared with those obtained by heating in H_2 and H_2S described earlier (4). Since pillared clays usually show only broad XRD patterns, the use of oriented specimens is helpful for measuring the basal spacing unambiguously. In addition to preferred orientation, XRD analysis using random orientation was also performed.

Figure 1 shows the XRD 2θ plots obtained for the mixed pillared montmorillonite and iron hydroxyoxide supported acid treated montmorillonite K-10 sulfided with CS_2. Unlike similar catalysts formed from sulfidation with H_2 and H_2S, XRD spectra did not show major lines corresponding to pyrrhotite or pyrite, as well as montmorillonite. Since sulfidation did occur, the iron sulfide species in these catalysts must be very minute.

Further characterization of the iron-pillared clays by acidity studies, IR, TGA, and Mossbauer spectroscopy is in progress and will be reported in our next quarterly.

3.3.3 Testing of Catalysts

3.3.3.1 Catalytic Hydrocracking of Bibenzyl

Since coal liquefaction can be carried out with a catalyst generated by adding ferric nitrate to coal and subsequently hydrolyzing to an iron hydroxyoxide form (7), a convenient method for generating an active catalyst may be the addition of ferric nitrate and subsequently ammonia to a clay and then mixing into the coal liquefaction slurry. Hydrocracking activities of iron hydroxy oxide or polyoxy triiron supported on commercial acid treated montmorillonite (K-10) and sulfided by heating with a 1000 psig mixture of H_2S and H_2 (10% H_2S) for 2 hours at 400°C were previously found to be very good. The high hydrocracking activity was attributed to the presence of strong acid sites (4). Also previous results with iron-pillared clays demonstrated that in situ sulfidation of the catalyst with small amount of carbon disulfide produced hydrocracking activity somewhat better than pre-sulfidation with H_2 and H_2S (4). In order to determine if the high hydrocracking activity can also be achieved by in situ sulfidation of iron supported on various clay precursors, catalysts prepared by addition of iron nitrate (followed by ammonium hydroxide treatment) to a commercial acid-treated clay (K-10) and Fe_3 complex by the incipient wetness method were tested with bibenzyl as the test compound. These catalysts were sulfided in-situ with CS_2 to convert the iron oxide or hydroxyoxide to pyrrhotite. These clays are not expected to be pillared, but contain very small particles of the active pyrrhotite when sulfided, as discussed above. The hydrotreating reactions were carried out by heating the substrate with catalyst at 350°C for 3 hours in the presence of small amount of CS_2 and 1000 psi of initial hydrogen pressure. Reaction conditions, conversion data, and major products are given in Table 1.

The reaction of bibenzyl with iron hydroxyoxide and triiron supported on K-10 gave 81 and 77% conversions, respectively. High resolution GC analysis indicated similar product distributions for these two catalysts (Table 1). 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. The ratio of benzene to ethylbenzene was 3-4, indicating the further cracking of the ethylbenzene to benzene. These products are indicative of the Bronsted acid catalysis mechanism (4).

The products included many hundreds of other components, indicative of rearrangements and hydrogen addition as well as hydrocracking. The 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. Some of the reaction products were addition products of bibenzyl that may be regarded as Friedel Crafts addition products, but higher molecular weight components were insignificant as indicated by GC analysis on a 15 m DB-5 column. These data indicate that extensive condensation (retrograde reactions) did not occur with these catalysts. The catalysts were recovered in almost quantitative amounts at the end of the reaction, and no retrograde reactions or coke were observed during reactions.

Compared with same catalysts sulfided in a separate step using a mixture of H_2 and H_2S, the conversion and product yields for the in situ sulfidation were somewhat lower. This effect is in the opposite direction from earlier studies with the mixed pillared clay catalysts. Since the magnitude of the difference in conversion is small, these data demonstrate that in situ sulfidation is a viable alternative to pre-sulfidation in a separate step. Further studies should provide more reliable data with respect to these sulfidation methods. The form of iron used in impregnating the clay is probably not important, but further studies are needed to determine if hydrolysis causes any differences in activity.

TABLE 1

CATALYTIC ACTIVITY OF IN SITU-SULFIDED IRON-IMPREGNATED CLAYS

Reaction Time = 3 hrs, Reaction Temp. = 350°C, H_2 = 1000 psig
Catalyst wt./Substrate wt. = 0.5

Catalyst (g)	BibenzyL (mmol)	Conversion (%)	Major Products (mmol)
K-10FeOOH Sulfided	2.90	81	Benzene (1.83) Toluene (0.27) Ethylbenzene (0.65) Methylcyclohexane (0.04) Ethylcyclohexane (0.01) Indan (0.05) Tetralin (0.09)
K-10Fe_3 Sulfided.	3.05	77	Benzene (1.56) Toluene (0.23) Ethylbenzene (0.37) Methylcyclohexane (0.02) Ethylcyclohexane (0.01) Indan (0.04) Tetralin (0.08)

3.3.3.2 Catalytic Hydrotreating of Model Compounds

Catalytic hydrotreating of pyrene and 1-methylnaphthalene were investigated to determine the activity of the sulfided supported as well as pillared clay catalysts for hydrogenation and hydrocracking of polynuclear aromatic systems common to most coals. Previous results have shown that iron hydroxy oxide supported on acid-washed montmorillonite, and pre-sulfided by heating with H_2 and H_2S is a moderate hydrogenation catalyst for pyrene. However, the hydrocracking activity was minimal under these conditions. The low hydrocracking activity was attributed to the absence of strong enough Bronsted acid sites, or else higher temperature may be needed for pyrene cracking (4). In order to determine if the in situ sulfidation can generate a mixed pillared clay-supported catalyst with activity better than obtained by presulfidation with H_2S and H_2, small amount of CS_2 was added to the catalyst for in situ sulfidation of the catalyst. Hydrotreating was carried out at 400°C for 3 hours in the presence of 1000 psi of hydrogen. The reaction was also carried out at 440°C to determine the hydrocracking activity of the catalyst. The activity of mixed pillared montmorillonite catalyst was then compared with NiMo (hydrogenation catalyst) supported on chromia-pillared clay. The reaction conditions, conversion data, and product distributions are given in Table 2.

TABLE 2

CATALYTIC HYDROTREATING OF PYRENE

Reaction Temp = 400°C, Reaction Time = 3 hrs, H_2 = 1000 psi
Catalyst wt./Substrate wt. = 0.5, CS_2 = 0.05

Catalyst	Temp. (°C)	Conv. (%)	Major Products (mmol)
DS-.21A.67IPC (Sulfided)	400	67	Hexadecahydropyrene (trace) (3 isomers) 1,2,3,3_a,4,5,9,10_a, 10_b-Decahydropyrene (0.04) c-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (0.03) t-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (0.04) 1,2,3,3_a,4,5-Hexahydropyrene (0.22) 1,2,3,6,7,8-Hexahydropyrene (0.29) 4,5,9,10-Tetrahydropyrene (0.07) 4,5-Dihydropyrene (0.44) Cracked Products 36%
DS-.21A.67IPC* (Sulfided)	440	50	Hexadecahydropyrene (trace) (3 isomers) 1,2,3,3_a,4,5,9,10_a,10_b-Decahydropyrene (trace) c-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (trace) t-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (trace) 1,2,3,3_a,4,5-Hexahydropyrene (0.07) 1,2,3,6,7,8-Hexahydropyrene (0.09) 4,5,9,10-Tetrahydropyrene (0.05) 4,5-Dihydropyrene (43) Cracked Products 47%
NiMoHCPC (Sulfided)	400	62	Hexadecahydropyrene (trace) (3 isomers) 1,2,3,3_a,4,5,9,10_a,10_b-Decahydropyrene (0.03) c-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (0.02) t-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene (0.04) 1,2,3,3_a,4,5-Hexahydropyrene (0.18) 1,2,3,6,7,8-Hexahydropyrene (0.24) 4,5,9,10-Tetrahydropyrene (0.07) 4,5-Dihydropyrene(0.45) Cracked Products 36%

The reaction of pyrene with the mixed pillared montmorillonite (DS.21.67IPC) gave a high conversion (67%) of pyrene into products. The majority of the products were di-, and hexa-hydropyrenes. Since we did not calibrate for these isomers, data are derived from FID assuming the response factors of pyrene and hydropyrenes to be the same. Relatively small amounts of hexdecahydro-, decahydro- and tetrahydropyrenes were also formed. The hydrogenation activity was similar to that of commercial catalysts such as Trilobe-HDN(Ni-Moly) catalyst and cobalt moly (AMOCAT) catalyst (8) at this temperature. Hydrogenation activity was also similar to that of iron hydroxyoxide supported on acid washed montmorillonite pre-sulfided with H_2S and H_2 (4), indicating the effectiveness of in-situ sulfidation with CS_2. It is important to note that with the in situ-sulfided catalyst, substantial amounts of lower molecular weight components (about 36% of the total products) were formed by hydrocracking and rearrangement reactions. The weight of the recovered catalyst was essentially the same as the initial catalyst, indicating no coking or retrogressive reaction had occurred with these catalysts. Hydrocracking to 1-, 2-, and 3-ring compounds was minimal under these conditions.

The reaction at 440°C gave a lower conversion (50%) of pyrene into products. Major products were di- and hexahydropyrenes. Small amounts of isomeric tetrahydropyrenes, decahydropyrenes and hexadecahydropyrenes were also formed. A large number of other products amounting to 22 wt.% of pyrene (47% of the total products) were also formed as a result of hydrocracking of pyrene. These data demonstrate increased pyrene cracking at higher temperature. Further work is in progress to develop catalysts and conditions suitable for hydrogen transfer as well hydrocracking of polynuclear aromatics.

The reaction of 1-methylnaphthalene was carried out with iron hydroxyoxide supported on K-10 and mixed alumina/iron pillared montmorillonite. Small amounts of carbon disulfide were added for in situ sulfidation of the catalysts. Hydrotreating was carried out at 300°C for 3 hours in the presence of 1000 psi of initial hydrogen pressure. These reactions gave very high conversions of 1-methylnaphthalene into products, 87 and 82% for mixed pillared and triiron supported K-10 respectively. Major products were 1- and 2-methylnaphthalenes, and 1-, 2-, and 5-methyltetralins. Relatively small amounts of tetralin, naphthalene, benzene, toluene, etc. were also formed. These products are indicative of rearrangement, hydrogenation and hydrocracking reactions occurring during hydrotreating. Mixed pillared montmorillonite gave somewhat better conversion and product distribution than the supported K-10 catalyst. Of major importance is the ratio of 1- to 2-methylnaphthalene and 1- to 2-methyltetralin obtained with the two catalysts tested. The ratios are quite a bit smaller for the pillared clay supported catalyst. This appears to be evidence for shape selectivity in the pillared clay reaction. The 2-methyl isomer is the favored product with the pillared clay catalyst owing to the smaller width of that isomer. If shape selectivity is occurring, then we can with more certainty that reactions are actually occurring in the interstitial spaces of the clays, not just on the outside surfaces.

TABLE 3

CATALYTIC HYDROTREATING OF 1-METHYLNAPHTHALENE

Reaction Temp. = 300°C, Reaction Time = 3 hours, H_2 = 1000 psi
Catalyst wt/Substrate wt = 0.5, CS_2 = 0.05 g

Catalyst	Substr. (mmol)	Conv. (%)	Major Products (mmol)
K-10FeOOH (Sulfided)	1-MENP (3.61)	82	2-Methylnaphthalene (0.68) 1-Methyltetralin (0.42) 2-Methyltetralin (0.54) 5-Methyltetralin (0.43) Cracked Products = 23% 1-/2-Methylnaphthalene = 0.94
DS-.21A.67IPC (Sulfided)	1-MENP (3.80)	87	2-Methylnaphthalene (0.65) 1-Methyltetralin (0.42) 2-Methyltetralin (0.72) 5-Methyltetralin (0.43) Cracked Products (27%) 1-/2-Methylnaphthalene = 0.74

3.3.3.3 Catalytic Liquefaction of Wyodak Coal

Cugini and co-workers have reported that a catalyst generated by adding ferric nitrate to coal and subsequently hydrolyzing to an iron hydroxyoxide form gave improved conversion of high rank coals at 425°C for 1 hour contact time (7). These catalysts, however, lack strong Bronsted acid sites required for effective depolymerization of coal under liquefaction conditions. In order to investigate if acidic supports can improve the conversion of low-rank coals to distillate fuels, iron hydroxyoxide was generated on acid treated montmorillonite (K-10) support in a separate step and then slurried with coal and solvent. Hydrotreating of bibenzyl with iron hydroxyoxide supported on Na-montmorillonite (weak Bronsted acid sites) and acid treated montmorillonite K-10 (strong Bronsted acid sites) indicated very poor cracking activity for Na-montmorillonite support (9) and very high activity for acid treated montmorillonite (4). Thus in addition to iron sulfides, strong acid sites are also needed. Another important advantage of generating iron hydroxyoxide on acid supports is that the resulting pyrrhotite formed from sulfidation prevents the retrogressive reactions responsible for coke formation by transferring hydrogen to the carbonium ions formed from the acid-catalyzed bond cleavages.

Since high conversions to THF solubles are easily obtained at 400°C without any promoter or catalyst with the low-rank coals (10), the conversion to oils, asphaltenes, and distillate needs to be accurately determined. The composition of the distillate or oils and asphaltene products obtained from the catalytic reactions must be determined in order to determine the effects of catalysts on coal liquefaction. The reaction of Wyodak subbituminous coal was conducted with iron hydroxyoxide supported on K-10 at 425°C for one hour in the presence of 1000 psi of initial hydrogen pressure. A small amount of CS_2 was added for in-situ sulfidation of the catalyst. The product slurry was separated into THF insolubles, THF solubles, toluene solubles, and pentane soluble fractions. THF insoluble, THF soluble and toluene soluble products were dried and weighed. The conversion and product yields are given in Table 4.

The weight of the THF insoluble product was used to determine the conversion of coal into soluble products. Percent conversion was calculated on the basis of the maf coal that did not appear in the this fraction. This catalyst gave very high conversion (93%) of the coal into soluble products. The yields of THF solubles were 9%, toluene solubles were 17%, and oil/gases/water were 67%, with a total conversion to soluble products of 93%. The pentane solubles consisted of coal-derived oil as well as solvent and solvent-derived materials; therefore, the oil yield was determined by the difference between the isolatable products described above and the maf coal weight converted into products (thus the amount includes gases and reaction product water). The composition of the oil product was determined by gas chromatography of the pentane/tetralin solution. This analysis showed that the coal-derived oil product consisted of 12% phenolics and 42% hydrocarbons, based on maf coal. This product quality is better than previously attained with this coal in a 1-hr single-stage run.

A similar reaction of Wyodak coal with discrete alumina/iron-pillared montmorillonite catalyst was also conducted to investigate if large micropore structure can be more effective in coal conversion. As before, the product slurry was separated into THF insolubles, THF solubles, and toluene solubles. The conversion of coal into soluble products was found to be 90% (Table 4). The yields of THF solubles, toluene soluble and pentane soluble products were 19%, 25% and 46% respectively, with a total conversion to soluble products of 90%. High resolution GC analysis indicated that the pentane soluble product consisted of 9% phenolics and 25% hydrocarbons (11). These data indicate that compared with the supported catalyst described above, the pillared clay catalyst gave lower conversion as well as inferior product quality. Although an exact explanation for the lower activity of the pillared clay catalyst is not possible at this time, Bronsted acidity, pore plugging and inaccessabilty of the pyrrhotite within the clay layers may have contributed to lower conversion.

TABLE 4

LIQUEFACTION OF WYODAK COAL

Reaction Temp. = 425°C, Reaction Time = 1 hr, H_2 = 1000 psi
Catalyst wt/Coal wt. = 0.1, Coal wt./Solvent wt. = 0.5

Catalyst	Coal (g)	Conv.* (%)	Products (%)		
			Toluene-S	THF-S	Pentane-S#
K-10FeOOH	7.0	93	17	9	67
DS-.21A.67IPC	7.14	90	25	19	46

* = conversions are based upon the amount of the initial coal (maf)
# = Pentane solubles are by difference, also includes gases and water formed during reaction

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