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FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

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by

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EXECUTIVE SUMMARY

The mixed iron/alumina pillared clay catalysts and clay-supported iron catalysts have been shown in previous reports of this project to significantly improve yields of heptane-soluble products obtained in the liquefaction of both as received and acid-exchanged Wyodak subbituminous coal and Blind Canyon bituminous coal. In these liquefaction reactions, several changes occur, including breakdown of the gel structure and solubilization, hydrogenation of the coal structures, and depolymerization of the coal macromolecules. Further tests of the catalysts were desired which focus mainly on the hydrogenation and depolymerization reactions. In this quarter, therefore, the soluble product (LSW) obtained from the noncatalytic low-severity liquefaction of Wyodak coal was used as a feed to determine the activity of iron based catalysts for the hydrogenation and depolymerization steps. The thermal noncatalytic reaction of LSW at 425°C for one hour in the presence of 1000 psi of H_2 gave 15% conversion of the LSW to oils. The catalytic liquefaction of LSW using sulfided mixed iron/alumina pillared montmorillonite gave significantly higher conversions: 30% conversion to oils in one hour and 42% conversion to oils in 3 hours.

Comparison data for liquefaction of the soluble LSW with other catalysts were desired, and these data were obtained for a dispersed form of iron sulfide, prepared via iron hydroxyoxide (PETC method). The iron oxyhydroxide catalyst was directly precipitated on LSW product using either water or ethanol as the solvent. LSW impregnated with iron hydroxyoxide in water gave a conversion similar to that for thermal reaction. However, impregnating LSW with iron hydroxyoxide in ethanol improved the conversion to oils to 28%. This result actually demonstrates a new viable method for liquefaction, because the dispersed catalyst utilized in this way is not deactivated as it is in the liquefaction of raw coal where the high calcium content can cause rapid sintering or blocking of the catalyst sites. Even more effective was the liquefaction of LSW with the soluble iron oxoaluminate precursor discussed below.

An insight into the functioning of the mixed iron/alumina pillared clay in coal liquefaction was investigated by preparing and studying an iron oxoaluminate structure. An investigation of new methods for the production of tetralin-soluble iron oxometallate catalysts and the determination of their catalytic activities was continued in this quarter. The hydrogenation activity of iron oxoaluminate was investigated using pyrene and 1-methylnaphthalene as the test compounds, and results were compared with thermal reactions. Iron oxoaluminate gave very high conversion of pyrene into hydropyrenes. In order to determine the loss of activity, recovered catalyst was recycled a second time for the hydrotreating of pyrene. Recovered catalyst gave similar conversion and product distribution as the original catalyst. Reaction of 1-methylnaphthalene with iron oxoaluminate also gave very high conversion to 1- and 5-methyltetralins and small amount of 2- and 6-methyltetralins.

Liquefaction of Wyodak subbituminous and Blind Canyon bituminous coal was investigated using an in situ sulfided soluble iron oxoaluminate catalyst. Compared with thermal reaction, iron oxoaluminate catalyst gave a significantly larger conversion of the Wyodak coal to heptane-solubles (oils). Improvement in the conversion was somewhat smaller for Blind Canyon coal. The reaction of LSW with soluble iron oxoaluminate gave higher conversion to oils than other catalysts.

Previous work in this project showed that high hydrocracking activity can be achieved with 10 wt.% of iron supported clays. Since high surface area solids are sought for coal liquefaction, we investigated fine Degussa silica particles (fumed silica and fumed alumina) with added aluminate as a support for generating supported iron catalysts. Degussa silica itself showed no hydrocracking activity for bibenzyl. Activation of Degussa silica with polyoxyaluminum cations showed only a small increase in the activity, indicating a lack of exchangeable cations that should have resulted from the polyoxyaluminum treatment. Alternatively, aluminosilicates were incorporated into the Degussa silica by treating with sodium aluminate followed by washing with ammonium nitrate to remove sodium ions. This procedure also failed to impart a high acidity to the catalyst and catalysts resulting from impregnation of triiron complex were not very active. Another type of silica/alumina support material was obtained by hydrolyzing silica/aluminum chloride complex by exposing to air or 5% Na_2CO_3 until all chlorides are lost. The resulting product was impregnated with iron hydroxyoxide using the PETC method. Iron hydroxyoxide impregnated on Na_2CO_3-hydrolyzed silica/aluminum chloride showed no hydrocracking activity, but use of a support produced by hydrolysis in air showed some promise. Presently none of these catalysts are comparable in activity with the clay-supported catalysts.

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.

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 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. (2). Detailed procedure has been described in the previous quarterly report (3).

3.2.1.2 Preparation of pillared clay catalysts

Iron/alumina pillared clay was prepared with ethanol drying according to the procedure described in our previous report (4)

3.2.1.3 Preparation of iron oxoaluminate

Iron oxoaluminate tetraisoproxide was prepared by a procedure similar to that reported by earlier by Ouhadi and others (5). In a 100 ml round bottomed, 10 g anhydrous tetralin was placed. The flask was attached to a N_2 inlet tube, a condenser and a receiving flask. The distillation assembly was flushed with N_2 to displace air. Aluminum isopropylate (2.04 g) and anhydrous iron(II) acetate were added to the flask, and stirred for 15 minutes. The reaction mixture was heated until distillation of isopropyl acetate was over. The green solution thus obtained was stored under nitrogen.

3.2.1.4 Preparation of Degussa silica-supported catalysts

SIDS Degussa silica (2 g) was stirred with 150 ml water for 15 minutes. A warm solution of 0.62 g $Fe_2(SO_4)_3.nH_2O$ in 20 ml water was added to the silica suspension and stirred for 15 minutes. Ammonium hydroxide (8 g) in 100 ml deionized water added to the beige color suspension and stirred for 15 minutes. The dark orange suspension was separated by centrifugation and washed with water. The product was vacuum dried at 110°C followed by calcination at 500°C for 3 hours. The dried silica-supported sulfated iron (SIDS) catalyst was packed in a glass tube, and vapors of argon saturated with water were passed over the catalyst for several hours. The "rehumidified" catalyst was kept under Argon for further use.

POADS Degussa silica-supported polyoxyaluminate catalyst (POADS) was prepared by a procedure similar to that described in our previous reports for alumina-pillared clays (10-13). Degussa aerosil mox80 (fumed silica and fumed alumina, surface area 220-270 m^2/g) obtained from Aldrich Chemical company was used as a support without further purification. In a round bottomed flask, 5.0 g of silica was suspended in 1000 ml deionized water. Al_{13} solution (300 ml) prepared by hydrolyzing 0.02M solution of $AlCl_3$ with 0.5N NaOH solution was added dropwise to the silica suspension, and stirred for 30 minutes. Excess solvent was then removed by evaporation. The resulting solid was dried in vacuum at 35°C for 6 hours and calcined at 350°C for 6 hours. The calcined product was washed with water to remove sodium ions. The product was dried at 35°C and recalcined at 350°C for 6 hours.

Iron hydroxyoxide was supported on polyoxyaluminum-treated Degussa silica (POADS) prepared above according to the procedure reported for iron hydroxyoxide on K-10 (4).

ADS To form an acidic aluminosilicate layer on the Degussa silica, 1 g of the particles were stirred overnight with a solution of 2 wt% of $NaAlO_2$. The product was washed with water and then with NH_4NO_3 prior to calcination.

TI-ADS-1 A similar batch of ADS particles were prepared by stirring the silica with 2 wt% solution of $NaAlO_2$. The product was washed with deionized water and exchanged with triiron complex to exchange iron for the sodium. The product was washed with ethanol prior to calcination.

TI-ADS-2 Degussa silica (1.0 g) was heated with a solution of $NaAlO_2$ (0.5 g) in 50 ml deionized for several hours. The product was separated by centrifugation and washing with deionized water. This product was exchanged with triiron complex as described earlier (4). The exchanged product was washed with ethanol and calcined at 350°C for 3 hours.

TI-ADS-3 Degussa silica (1.0 g) was stirred with a solution of 0.032 g of $NaAlO_2$ (corresponding to 2 wt% Al_2O_3). Excess solvent was removed by evaporation and the product calcined at 500°C for 3 hrs. The calcined product was exchanged with triiron complex according to the procedure described in our previous quarterly reports (4). The exchanged product was washed with ethanol prior to calcination at 350°C for 3 hours.

IAS-2 A solid acid catalyst was prepared by heating anhydrous aluminum chloride and silica in chloroform according to the procedure reported by Drago and coworkers (6). A portion of this catalyst was exposed to atmosphere for several hours until the color changed from yellow to white. The air exposed catalyst was used aa a support for iron hydroxyoxide using the PETC method (7).

IAS-1 In another similar experiment, the solid acid catalyst was hydrolyzed by treating with 5% Na_2CO_3. The hydrolyzed catalyst was used as a support for iron hydroxyoxide using the PETC method (7).

3.2.1.5 Sulfidation of catalysts

All the catalysts used in these investigations were in situ sulfided. A small amount of elemental sulfur was added along with the catalyst prior to hydrotreating.

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 recovered iron oxoaluminate is ground with water and smeared onto a single crystal, "zero"-background, quartz plate to obtain an oriented specimen so as to give intense 001 basal reflections. Diffraction data are collected in 0.02° steps for one second dwell time using a Phillips automated diffractometer equipped with a copper tube, theta-compensating slit, graphite diffracted beam monochromator, and scintillation detector. Software programs supplied by Materials Data Inc. are used for data collection, data reduction, and phase identification.

3.2.3 Catalytic Hydrotreatment of LSW Products

Preparation of the LSW (low-severity liquefaction product from liquefaction of Wyodak coal in tetralin with CO-H_2S) has been reported elsewhere (8).

A slurry consisting of 1.0 g of LSW or catalyst impregnated LSW, 10 wt % desired catalyst if needed, 2 wt% g of elemental sulfur, and 2 g of tetralin (solvent) were placed in a 70-ml Parr reactor. For the reaction of LSW with iron oxoaluminate, a slurry consisting of 1.0 g LSW and 2.0 g iron oxoaluminate in tetralin along with 2 wt% of elemental sulfur was used. For the reaction of LSW obtained from CO-Water liquefaction (table), a slurry of 3 g LSW, 10 wt% of desired catalyst, 2 wt% of sulfur and 3 hours reaction time was used. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for 60 minutes. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with tetrahydrofuran (THF). The THF-insoluble product was dried under vacuum and weighed. The extract was diluted to 250 ml with THF. A 4 ml aliquot of the THF-soluble was mixed with one ml solution of internal standard (a mixture of 2,2,4-trimethylpentane and n-octadecane in dichloromethane) and analyzed by GC. The remaining THF-soluble was evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. The percent conversion was calculated on the basis of the heptane-insoluble product was converted to heptane-soluble product (oils). The conversion and yield data are given in Tables 4 and 5.

3.2.4 Preparation of FeOOH-Supported LSW

Low-severity Wyodak liquefaction product (LSW) was treated by PETC method (7). The LSW (2 g) was suspended in 30 ml water. A solution of 0.10 g $Fe(NO_3)_3.9H_2O$ in 10 ml water was added to the LSW suspension, and stirred. A solution of 2 g NH_4OH in 15 ml water was added to this slurry and stirred for 30 minutes. The residue was separated by centrifugation, washed with water and finally with ethanol. The residue was dried in vacuum at 40°C for 16 hours.

LSW was also treated by above method using ethanol as the solvent. Pretreated LSW product was dried in vacuum at 40°C for 16 hours.

3.2.5 Catalytic hydrotreating of Model Compounds

In a typical run, 0.50 g of the test compound, 10 wt% of the desired catalyst and equivalent amounts of elemental sulfur (for in-situ sulfidation of catalyst) were placed in a 15 ml microreactor (tubing bomb). The microreator was evacuated and pressurized with 1000 psi of hydrogen, and placed in a rocking heater 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 and weighed.

3.2.6 Liquefaction of Coals

A slurry consisting of 10.0 g of coal (as received Wyodak-Clovis Point) or Blind Canyon, 0.05 mole of $NaAlO_2$ (if desired) dissolved in 6 g water and 10 g of tetralin (solvent) were placed in a 70-ml Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of carbon monoxide gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The reactor was attached to a set of traps cooled in dry ice-acetone slurry, and distilled to remove water. The remaining product slurry was extracted with tetrahydrofuran (THF). The THF-insoluble product was dried under vacuum and weighed. The extract was evaporated to remove THF. The resulting slurry was stored under nitrogen for further hydrotreating with catalysts.

A 3.g aliquot of THF-solubles was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. 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 Tables 4 and 5.

3.3 Results and Discussion

3.3.1. Catalytic Liquefaction of Soluble Low-Severity Products

Various iron catalysts have been effective in improving yields of soluble products from coals. Coal liquefaction can also be carried out with a dispersed catalyst generated by adding ferric nitrate to coal and subsequently hydrolyzing to an iron hydroxyoxide form (7). This catalyst has been found to improve the liquefaction of high-rank as well as low-rank coals. However, liquefaction of low-rank coals is impeded by the mineral content of the coal. Inorganic constituents such as calcium are a major factor in deposits in the process equipment, but they also disrupt the functioning of the catalyst by blocking pores, deactivating sites, or causing sintering or aggregation. In order to overcome these problems, Wyodak coal was solubilized by heating in tetralin at 380°c for one hour in the presence of 1000 psi (cold) mixture of H_2S and CO (10% H_2S). This gave a ash free intermediate (LSW) which was then catalytically hydrotreated using a variety of catalysts. The reaction was carried out by heating the low-severity product with 10 wt% of the catalyst at 425°C for 1 hr in the presence of 1000 psi of initial (cold) hydrogen pressure. A small amount of sulfur was added to the reactor for in situ sulfidation of the catalyst. Reaction conditions and conversion data are given in Table 1.

Several reactions of a mineral free low-severity intermediate from Wyodak coal (LSW) were carried out with various catalysts to determine their catalytic activity. A THF-soluble intermediate was obtained by thermal liquefaction in CO and H_2S 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. The LSW is a low-density solid at ambient temperature, but melts easily. A thermal (noncatalytic) reaction of the LSW gave 15% conversion of the heptane-insoluble to heptane-solubles (oil). The 15% value for the LSW represents a conversion of preasphaltenes and asphaltenes to heptane-soluble oils.

The liquefaction reaction of the LSW in tetralin with the dispersed iron/alumina-pillared clay catalyst (in situ sulfided) gave 30% conversion to heptane-solubles under the same conditions. The two-fold increase in conversion to oils for catalytic versus thermal reaction of LSW substrate thus compares favorably with the increase of 6% (48% to 54%) found in the experiments of as-received versus ion-exchanged Wyodak coal (9). However, when the same reaction was carried out for 3 hours, conversion increased to 42% (Table-1).

The LSW intermediate was also subjected to the PETC iron dispersion treatment by stirring the low-density solid LSW with ferric nitrate solution and adding ammonium hydroxide to generate the surface-bound iron hydroxyoxide (FeOOH) (7). Reaction of FeOOH-impregnated LSW gave only 14% conversion to oils, which is almost the same as than obtained for noncatalytic reaction. Hydrophobic nature of the low-severity product may have prevented the effective impregnation of the FeOOH into LSW. Alternatively, a variation of the PETC method was attempted to generate the dispersed iron catalyst on the LSW. Ethanol was used as to obtain a colloidal dispersion of the LSW, which was then mixed with the ferric nitrate solution in ethanol followed by addition of ammonium hydroxide. After removal of ethanol, the liquefaction was carried out in tetralin under conditions similar to those obtained above. When the dispersed iron obtained by this method was utilized, a 28% yield of the heptane-soluble oils was obtained. It is now obvious that there are critical interactions between the iron and the coal surface that need to be further understood and evaluated for designing a viable coal liquefaction method. A soluble form of iron catalyst was obtained by heating iron(II) acetate with aluminum isopropylate in tetralin. This reaction forms iron oxoaluminate via the elimination of isopropyl acetate. LSW was reacted with the solution of iron oxoaluminate in tetralin under above condition to determine the effect of homogeneous catalyst on the yield of oils. This reaction gave very high conversion (54%) conversion of heptane-insoluble product to oils.

Table 1

Liquefaction of Low-Severity Wyodak Products

Reaction temp. = 425°C, Reaction Time = 1 hr
H_2 = 1000 psi (cold)

LSW (g)	Catalyst (wt.%)	Solvent (g)	Heptane-I (g)	Heptane-S (g)	Conv. to Hept-S (%)
1.0	None	Tetralin (2)	0.85	0.15	15
1.0	FeOOH^a (1) Sulfur (1)	Tetralin (2)	0.86	0.14	14
1.01	FeOOH^b (1) Sulfur (1)	Tetralin (2)	0.73	0.28	28
1.0	APC-Fe_3^* (10) Sulfur (2)	Tetralin (2)	0.70	0.30	30
1.0	APC-Fe_3^* (10) Sulfur (2)	Tetralin (2)	0.58^c	0.42	42
1.01	IOAl (25) Sulfur (2)	Tetralin (1.8)	0.47	0.54	54

a = PETC method in water.
b = PETC method in ethanol.
c = three hours reaction.
* = ethanol dried mixed pillars Iron/alumina pillared montmorillonite.

3.3.2 Homogeneous (iron oxoaluminate) catalyst

3.3.2.1 Hydrogenation of model compounds

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 oxometallate groups attached to the transition metal precursor. The oxometallate groups are intended to form a stabilizing matrix around the transition metal site in the active catalyst. A close resemblance to the mixed iron/alumina pillared structures formed is expected. Thus a insight into the functioning of the mixed pillar structures might be sought by examining the chemistry of the iron oxometallates. Early studies of these catalysts have been directed to both fundamental questions of reactivity and mechanism as well as direct coal liquefaction.

Iron oxoaluminate tetraisopropoxide (5) was generated by heating ferrous acetate and aluminum isopropylate in tetralin in a stream of dry nitrogen. Distillation of isopropyl acetate formed during reaction gave a green solution of iron oxoaluminate in tetralin.

Iron oxoaluminate tetraisopropoxide was heated with a small amount of sulfur at 400°C for 2 hours in the presence of 1000 psi of hydrogen (cold pressure). The reaction product was extracted with heptane and a black precipitate was separated by centrifugation, and dried in vacuum at 50°C. A very low-density black powder was obtained. This product was analyzed by diffuse reflectance FTIR and X-ray diffraction spectroscopy. Infrared data indicated the loss of isopropyl groups upon heating with sulfur. In the XRD data only pyrrhotite could be identified. No peaks corresponding to alumina was observed, which may indicate amorphous nature of the alumina in the heated catalyst.

A series of reactions was carried out with the sulfided iron oxoaluminate in tetralin at 400°C to determine whether catalytic activity exists for aromatic ring reduction. The reaction of pyrene and 1-methylnaphthalene were carried with and without iron oxoaluminate in tetralin at 400°c for 2 hours in the presence of 1000 psi of H_2 (cold) and a small amount of sulfur for in situ sulfidation of iron. Reaction conditions and conversion data are given in table-2.

The thermal noncatalytic reaction of pyrene gave very poor conversion (6%) to dihydropyrene. However when the hydrogenation was carried out in the presence of iron oxoaluminate and a small amount of sulfur, a very high conversion of pyrene (67%) was obtained. Major products were di-, tetra- and hexahydropyrenes along with a small amounts of decahydropyrenes (3-isomers). The catalyst recovered from this reaction was recycled to determine the loss of activity during hydrotreatment. Reaction of pyrene with recovered catalyst gave almost identical conversion and product distribution as that obtained with fresh catalyst. This data indicate that no loss of activity occurs during hydrotreatment despite the loss of isopropyl groups, as indicated by the IR data of the recovered catalyst.

The thermal reaction of 1-methylnaphthalene in tetralin showed only 25% conversion of the substrate to 1-methyltetralin. The reaction of 1-methylnaphthalene with iron oxoaluminate and sulfur gave very high conversion of the substrate to methyltetralins. Major products were 1- and 5-methyltetralins, and a small amount of 2- and 6-methyltetralins were also formed. The low yields of 2- and 6-methyltetralin, naphthalene, and tetralin demonstrate the low hydrocracking activity of this catalyst.

Table 2

HYDROGENATION ACTIVITY OF IRON OXOALUMINATE (IOAl)

Reaction Temp. = 400°C, Reaction time = 2 hrs, H_2 = 1000 psig, S = 0.03 g			
Catalyst (wt.%)	Substrate (mmol)	Conversion (%)	Major Products (mmol)
None	Pyrene (2.48)	6	DHP (0.11)
IOAl (10)	Pyrene (2.52)	67	DIHP (0.51) HHP1 (0.42) HHP2 (0.28) THP (0.10) DEHP1 (0.05) DEHP2 (0.04) DEHP3 (0.04)
IOAl* (10)	Pyrene (2.52)	66	DIHP (0.75) HHP1 (0.24) HHP2 (0.17) THP (0.16) DEHP (0.04)
None	1-Menaph (3.50)	2	1-Methyltetralin (0.02)
IOAl (10)	1-Menaph (3.52)	77	5-methyltetralin (1.46) 1-Methyltetralin (1.12) 2-Methyltetralin (0.02) 6-Methyltetralin (0.02)

IOAl = Iron oxoaluminate solution in tetralin.
* = Mixture of recovered Iron oxoaluminate and tetralin

3.3.2.2 Iron oxoaluminate-catalyzed coal liquefaction

Iron oxoaluminate showed considerable hydrogenation activity for pyrene and 1-methylnaphthalene (3.3.1.2). Iron oxoaluminate tetraisopropoxide is soluble in tetralin, and thus can be used as a homogeneous catalyst for liquefaction of coals or first-stage liquefaction products. A series of tests with Wyodak and Blind Canyon coals in tetralin (coal/solvent = 0.5) with and without iron oxoaluminate were conducted at 425°C for 1 hour and 1000 psi of initial hydrogen gas. A small amount of elemental sulfur was added to the reaction mixture for in situ sulfidation of the iron catalysts. The reaction conditions and conversion data are given in table-3.

Table 3

Coal Liquefaction Results

Reaction Temp = 425°C, Reaction Time = 1 hr, Sulfur (wt%) = 2 H_2 = 1000 psi (cold)					
Coal (g)	Catalyst (wt.%)	Solvent (g)	Conversion (%)	Heptane-I (%)	Heptane-S (%)
Wyodak (7)	None	Tetralin (14)	89	41	48
Wyodak (7.1)	IOAl (15)	Tetralin (10)	94	34	60
Blind Canyon (5.4)	None	Tetralin (10)	91	58	33
Blind Canyon (5.5)	IOAl (15)	Tetralin (10)	91	40	51

IOAl = Iron oxoaluminate

Noncatalytic (thermal) reaction of ARW coal gave 89% conversion of coal to THF-soluble products, with 48% being heptane-solubles (oils) products Since high conversions to THF-solubles are easily obtained at 400°C without any catalyst with the low-rank coals, the conversion to oils and asphaltenes was accurately determined to evaluate the activity of the catalysts. Reaction of Wyodak (as received) with iron oxoaluminate and sulfur added gave a 6% higher conversion (94%) to THF-soluble products than the thermal reaction. The most significant improvement for the in situ sulfided iron oxoaluminate catalyst was the increase in the oil fraction (60%). These data are consistent with the observed hydrogenation activity of this catalyst for model compound reaction (Table-2).

Conversion to THF solubles with as received Blind Canyon (high volatile bituminous) coal without catalyst (thermal reaction) was somewhat higher (91%) than Wyodak coal. However, the conversion to heptane-soluble products was much lower than Wyodak coal under the same conditions. The reaction using iron oxoaluminate and a small amount of sulfur gave the same conversion into THF-soluble products for this coal. As in the case of Wyodak, a major improvement was observed in the conversion to oils. The composition of the oils for thermal reactions as well as catalytic liquefaction are currently being determined.

3.3.3 Fine Aluminosilicate Particle-Supported Iron Catalysts

Inexpensive catalysts with high surface area, strong acidity, and hydrogen transfer activity are believed to be ideal candidates for coal liquefaction and depolymerization. The objective in this project was to impregnate iron on nanoparticles of clay to as to utilize the acidic sites of the clay to assist in depolymerization of the coal macromolecules. Because of the tendency of the highly acidic iron and alumina pillared clays to agglomerate during the ion exchange step in the preparation, it was never possible to maintain the size of the clay particles in the 1-100 nm range, such as those present in the original sodium montmorillonite form. The iron sites in the clay catalysts are believed to be of this dimension, although the clay particle dimensions are in the 1 micron range. Other acidic supports are available in this size range and could serve as the support for an iron catalyst. Thus a second methodology to achieve the desired objective was attempted.

Degussa aerosil mox 80 (fumed silica and fumed alumina) is a very low-density and high surface area (220-270 m^2/g) solid. However, it does not activate hydrogen and lacks strong acid sites. A variety of techniques were used to introduce strong acid sites as well as hydrogen activators into Degussa silica particles. Hydrocracking activities of modified Degussa silica catalysts were investigated by heating bibenzyl and catalyst and a small amount of sulfur (for in situ sulfidation) for 3 hours at 350°C in the presence of 1000 psi of H_2 (cold pressure). Reaction conditions and conversion data are given in table-4.

Reaction of bibenzyl with 10 wt% of the unmodified Degussa silica (DS) gave very poor conversion (1%), and a trace of toluene was the only product. The poor hydrocracking activity on silica is typical of a lack of strong acid sites on the catalyst surface.

Degussa silica was treated with ferric sulfate and ammonium hydroxide in an adaptation of the procedure reported by Wender and coworkers (10) for preparing sulfated iron catalysts. The resulting silica-supported sulfated iron catalyst (SIDS catalyst) was rehumidified by passing vapors of argon saturated with water. Reaction of bibenzyl with this "rehumidified" catalyst gave very poor conversion (4%) to mainly benzene and toluene.

In order to create strong acid sites on the silica particles, Degussa silica was treated with polyoxyaluminum cations, similar to those used for pillaring reactions of clays. The reaction of bibenzyl with polyoxyaluminum-treated Degussa silica (POADS catalyst) gave only slightly higher conversion (8%) of the bibenzyl into toluene and benzene. The higher proportion of benzene is indicative of Bronsted acid-catalyzed hydrocracking, but the low conversion indicates that the oxyaluminum cation-treated Degussa silica either was not acidic enough to generate much hydrocracking activity or were not incorporated in sufficient numbers due to lack of exchangeable cations in the starting silica.

Aluminosilicate groups on the Degussa silica particle surface were generated by treating with a aqueous solution of sodium aluminate at ambient temperature. After washing with water, the particles were exchanged with triiron complex, washed with ethanol, and calcined at 350°c for 3 hours. The reaction of bibenzyl with this catalyst (TIADS-1) gave only 6% conversion to benzene and

Table 4

CATALYTIC REACTIONS WITH FINE SILICA CATALYSTS

Reaction Temp. = 350°C, Reaction Time = 3 hrs, Sulfur = 0.10 g, H_2 = 1000 psig

Catalyst (wt.%)	Sulfur (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
DS (10)	None	2.80	1	Toluene (trace)
SIDS (10) "Rehumidified)	4	2.75	4	Benzene (0.05) Toluene (0.01)
POADS (10)	None	2.75	8	Benzene (0.20) Toluene (0.04)
TI-ADS-1 (10)	4	2.88	6	Benzene (trace) Toluene (0.20)
TI-ADS-2 (10)	4	2.75	4	Benzene (0.03) Toluene (0.04)
TI-ADS-3 (10)	4	2.75	1	Benzene (trace) Tolene (trace)
ADS (10)	None	2.75	1	Toluene (trace)
I-AS-1 (10)	2	2.86	<1	Benzene (trace) Toluene (trace)
I-AS-2 (10)	2	2.75	26	Benzene (0.33) Toluene (0.06) Ethylbenzene (0.17)

toluene. A second version of this catalyst was prepared by digesting the silica particles with aqueous sodium aluminate followed by triiron intercalation. This catalyst (TIADS-2) also gave very poor conversion of bibenzyl (4%). Sodium aluminate also was supported on silica by an incipient wetness method, and then intercalated with triiron complex. This catalyst (TIADS-3) gave virtually no increase in the hydrocracking activity of Degussa silica. The low activity of these catalysts was attributed to the lack of formation of any significant amount of aluminosilicate on the fumed silica particles, consequently there were few exchangeable groups and low acidity of the catalyst. This was demonstrated by treating the sodium aluminate treated particles with ammonium nitrate solution and then calcining to remove ammonium groups. The conversion of bibenzyl with this material (ADS) was 1%.

Drago and coworkers (6) reported the formation of a silica-aluminum chloride (solid acid catalyst) by heating silica with aluminum chloride. This solid acid catalyst was prepared and hydrolyzed with 5% Na_2CO_3 solution or by exposure to air for several days. These hydrolyzed catalysts were converted to an aluminosilicate-supported iron hydroxyoxide by treatment with ferric and ammonium hydroxide (7). Reaction of bibenzyl with iron hydroxyoxide supported on Na_2CO_3 hydrolyzed silica-alumina catalyst (in situ sulfided) (IAS-1) gave very poor conversion (<1%). However, the catalyst obtained by supporting iron hydroxyoxide on air hydrolyzed silica-alumina (in situ sulfided) (IAS-2) gave significantly higher conversion (26%) of bibenzyl to benzene and ethylbenzene, toluene being the minor product. The higher activity is probably due to the absence of sodium.

In conclusion, general methods for fine particle aluminosilicate-supported iron catalysts have been examined, and the hydrocracking activities of the fine particle silica catalysts are far inferior to that of clay-supported iron catalysts. This investigation showed that a route involving use of aluminum chloride to generate an acidic aluminosilicate surface is more promising than other methods. Further work is required to optimize this method. Hydrogenation activities of the fine particle silica-supported catalysts have not yet been investigated. Significant activity for hydrogenation is expected.

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