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FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

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by

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EXECUTIVE SUMMARY

An investigation of new methods for the production and utilization of tetralin-soluble iron oxometallate precursors for coal liquefaction catalysts was continued in this quarter. Further descriptions of the catalytic activities of the sulfided forms were obtained. The hydrogenation activities of catalysts derived from iron oxotitanate and cobalt oxoaluminate were investigated using pyrene as a the test compound, and results were compared with thermal reactions. The hydrogenation activity of iron oxotitanate was superior to other catalysts including iron oxoaluminate. The hydrogenation activity of cobalt oxoaluminate was similar to that of iron oxoaluminate reported in previous quarterly report. Previous testing with bibenzyl showed that the sulfided catalysts did not have high hydrocracking activities, owing to a lack of highly acidic sites.

The liquefaction of Wyodak subbituminous coal was investigated using in situ sulfided iron oxotitanate catalyst. Compared with the thermal reaction, the iron oxotitanate catalyst significantly improved the conversion of the Wyodak coal to THF-solubles (97%) as well as heptane-solubles (67%). These results are comparable to those obtained with cobalt-molybdenum catalyst.

In order to improve the usefulness of iron oxoaluminate as a liquefaction catalyst, iron oxoaluminate was supported on acid-treated montmorillonite (K-10). Supporting the iron oxoaluminate on an acidic support significantly improved the hydrogenation activity of iron oxoaluminate. The hydrocracking activity was increased by a large factor. Thus the aluminate and titanate structures surrounding the pyrrhotite that forms during sulfidation have a beneficial effect in preventing deactivation of the iron sites, and the presence of the acidic sites in the clay results in effective catalytic synergism between catalyst and support. These clay-supported iron oxometallates are highly promising catalysts for coal liquefaction.

Iron oxyhydroxide and triiron supported on acid-treated montmorillonite (K-10) were tested for the liquefaction of ion-exchanged Wyodak (IEW) to minimize effects of the coal mineral matter. Both sulfided catalysts gave very high conversions of coal to THF-soluble and heptane-soluble (oils) products. The activity of the catalyst from iron hydroxyoxide generated on K-10 was significantly better than that from triiron supported on K-10. The difference in activity may be due to the size of the iron particles in the two catalysts. Both catalysts were highly active in hydrocracking tests with bibenzyl, the triiron catalyst being a little more active.

Other investigations have shown that fine particles of sulfided magnetite or maghemite are active catalysts for coal liquefaction. Both these catalysts showed poor hydrocracking activity in tests with bibenzyl. The lack of hydrocracking activity could be attributed to the absence of acidic sites in these catalysts. In an attempt to generate acidic sites that could interact with the magnetite sites, the magnetite was directly precipitated on montmorillonite support. However, the clay-supported magnetite was unstable and converted to maghemite during washing to remove the sodium ions. This procedure restored the acidity of the catalysts as indicated by the high conversion of bibenzyl to lighter components. Further testing of the clay-supported maghemite is needed.

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.

Work in the ninth quarter continued preparation and testing of acid treated montmorillonite clays containing iron sulfides from various iron precursors. Hydrocracking and hydrogenation activities of several soluble iron oxometallates were determined. High surface area low-density iron oxides were also prepared and tested.

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 iron oxoaluminate tetraisopropoxide

Iron oxoaluminate tetraisopropoxide was prepared according to the procedure reported earlier (4). 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. The preparation of iron oxoaluminate tetraisopropoxide was also attempted in heptane, decane and hexadecane.

A similar procedure was used for the preparation of cobalt oxoaluminate isopropoxide and iron oxotitanate hexaisopropoxide. Cobalt oxoaluminate tetraisopropoxide was prepared by heating cobalt acac and aluminum isopropylate in tetralin, and iron oxotitanate hexaisopropoxide was prepared by heating a mixture of iron(II) acetate and titanium isopropoxide in tetralin.

3.2.1.3 Preparation of Magnetite and Maghemite

Magnetite (Fe_3O_4) was prepared according to the procedure described elsewhere (5). A 10 g portion of the black solid was calcined at 250°C for 6 hours. A rust colored powder (maghemite) was obtained.

3.2.1.4 Preparation of Supported Catalysts

The procedure for the preparation of iron hydroxyoxide supported on acid-treated montmorillonite (K-10FeOOH) in ethanol as well as in water has been described elsewhere (6). Triiron-supported K-10 (K-10Fe_3) was prepared by the incipient wetness method using ethanol as solvent (6).

Iron oxoaluminate was supported on K-10 according to the following procedure: Acid treated montmorillonite (1 g) was suspended in 100 ml pentane and stirred for 30 minutes. A solution of iron oxoaluminate tetraisopropoxide (4 ml) in tetralin was added to the slurry dropwise with vigorous stirring. After the addition of the iron oxoaluminate, the slurry was stirred for 30 minutes. The precipitate were separated by centrifugation and washed with pentane. The residue was dried in vacuum at 50°C (no calcination).

Maghemite was supported on acid treated montmorillonite (K-10) using two different procedures:

A. Acid treated montmorillonite (72.0 g) clay was suspended in 500 ml deionized water. Nitrogen was bubbled through the solution along with stirring. Iron(II) sulfate heptahydrate (8.0 g) dissolved in 60 ml deionized water added to the clay suspension, and the slurry was heated to 90°C. A solution of 0.65 g KNO_3 and 4.5 g KOH was added dropwise to the above slurry with stirring. A black precipitate formed and the whole solution turned bluish green. Heating was continued for 60 minutes. The black solid was separated by centrifugation and washed several times with deionized water. The product was dried in vacuum. A 5.0 g portion of the black powder was calcined at 350°c for 3 hours to give a light tan powder. A 4.0 g portion of the black powder was washed with 50 ml of 10% acetic acid followed by washing with water to remove excess acetic acid, and dried in vacuum. As base was removed from the clay, the color was lost, indicating decomposition of the magnetite. The dried product was calcined at 350°C for 3 hours.

B. Alternatively, acid treated montmorillonite (9.0 g) clay was suspended in 100 ml deionized water. A solution of 0.6 g KOH in 20 ml deionized water was slowly added to the clay suspension with stirring followed by addition of a solution of 1 g iron(II) sulfate heptahydrate in 20 ml water. Upon addition of iron(II) sulfate the solution turned bluish green. The slurry was heated to 90°C. To this slurry, a solution of 0.08 g KNO_3 in 10 ml water was added while maintaining the pH of the solution at 10 using dilute KOH. The heating was continued for 60 minutes. The slurry was then cooled to room temperature. The solid was separated by centrifugation and washed thrice with deionized water. The product was dried in vacuum at 100°C.

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 Preparation of Ion-exchanged Wyodak (IEW)

As-received Wyodak coal (7 g) was stirred with 100 ml of 1N nitric acid for 1 hour. The solid coal was separated by centrifugation. The residue was washed with deionized water until free of acid. The ion-exchanged coal was dried in vacuum at 50°c overnight.

Ash contents of the ion-exchanged coal were determined in triplicate by heating 2 g sample of the coal. The coal was weighed in a porcelain crucible and the crucible was placed in a muffle furnace. The coal was heated at 110°C and held for 1 hour, at 400°C for 1 hour, and at 750°C for 4 hours. The weight of the residue was used to calculate percent ash in the ion-exchanged coal.

3.2.3 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). In reactions using iron oxoaluminate, iron oxotitanate and cobalt oxoaluminate catalysts, a 3 g solution of the catalyst in tetralin and small amount of sulfur was used. 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.

3.2.4 Liquefaction of Coals

A slurry consisting of 7.0 g of coal (as received Wyodak-Clovis Point), a solution of 15 wt% of iron oxotitanate in 10 g tetralin, 2 wt% of elemental sulfur for in situ sulfidation of catalyst were placed in a 70-ml Parr reactor. For the reaction of ion-exchanged Wyodak, 5 g IEW, 10 wt% of the desired catalyst, 2 wt% of elemental sulfur and 14 g of tetralin (solvent) were 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 evaporated to remove THF. The THF-soluble product 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.

3.2.5 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.

3.3 Results and Discussion

3.3.1 Hydrotreating of Model Compounds

3.3.1.1 Bibenzyl Hydrocracking

Catalysts with high surface area, strong acidity, and hydrogen transfer activity are needed for coal liquefaction. The clay-supported iron precursors for the catalysts we have previously prepared contained mixtures of iron oxides (maghemite and hematite). New methods for the formation of high surface area magnetite and maghemite have been reported recently. The preparation of magnetite supported on montmorillonite has not been reported, but it and other iron oxides supported on clays would be interesting to study in relationship to the clay-supported maghemite and hematite. The montmorillonite was treated with strong base and iron sulfate to generate magnetite on the clay support. Some of this material was heated to form a clay-supported maghemite. Fine particles of magnetite and maghemite were prepared for comparison with the clay-supported forms. Hydrocracking activities of these catalysts were investigated by heating bibenzyl with the 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-1.

Reaction of bibenzyl with 10 wt% of magnetite gave very poor conversion (3%), and a trace of benzene and small amount of toluene were the only product. Magnetite was calcined to convert it into maghemite. The reaction of bibenzyl with maghemite gave only slightly higher conversion (5%) of bibenzyl. Again a trace of benzene and small amount of toluene were the only products. The poor hydrocracking activity of these unsupported fine particle catalysts is indicative of the lack of strong acid sites on the sulfided catalyst surface.

Table 1

Catalytic Hydrocracking of Bibenzyl

Reaction Temp. = 350°C, Reaction Time = 3 hrs, Sulfur = 0.10 g, H_2 = 1000 psig			
Catalyst (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
K-10Fe_3 (10)	2.75	65	Benzene (1.38) Toluene (0.11) Ethylbenzene (0.40) Indan (0.02)
K10FeOOH (10)	2.75	61	Benzene (1.12) Toluene (0.10) Ethylbenzene (0.46) Indan (0.02) Tetralin (0.02)
K-10IOAl (10)	2.86	46	Benzene (1.26) Toluene (0.05) Ethylbenzene (0.78)
Magnetite (10)	2.75	3	Benzene (trace) Toluene (0.12)
Maghemite (10)	2.75	5	Benzene (trace) Toluene (0.10)
K-10Fe_2O_3 (B) (10)	2.86	4	Benzene (0.03) Toluene (0.09) Ethylbenzene (trace)
K-10$Fe_2O_3^*$ (A) (10)	2.75	57	Benzene (2.40) Toluene (0.08) Ethylbenzene (0.26)

* = washed with 10% acetic acid

Although a black magnetite deposit could be formed on montmorillonite in strong base, the montmorillonite-supported catalyst could not actually be prepared in an acidic form needed for the catalysis. Base used for the generation of magnetite on clay exchanged most of the acid sites with Na^+ ions. As expected, the sodium form of the catalyst gave a very poor conversion of bibenzyl. Washing to remove sodium ions converted the magnetite to other iron oxide forms.

An iron oxide (maghemite form) obtained after calcination of the montmorillonite-supported magnetite was acid-washed to remove sodium ions restore acidity. The reaction of bibenzyl with the acid-washed catalyst gave significantly higher conversion (57%) of bibenzyl into light components. Major product were benzene and ethylbenzene (cationic mechanism) along with a small amount of toluene. No coke or oligomeric products were formed, indicating the absence of retrograde condensation reaction.

The two most active catalysts in this project for coal liquefaction appeared to be those obtained by impregnation of K-10 with triiron complex and with ferric nitrate, followed by rapid drying. New batches of these montmorillonite-supported iron catalysts were prepared and tested with bibenzyl. The K-10 clay was impregnated with triiron complex in ethanol, and calcined at 350°c for 3 hours. The reaction of bibenzyl with 10 wt% of this catalyst gave only 65% conversion to benzene and ethylbenzene. Small amounts of toluene and ethylbenzene were also formed. Another supported catalyst was also prepared by supporting K-10 with iron hydroxyoxide in water using the PETC method (R). The catalyst was washed with ethanol prior to calcination. This catalyst gave 61% conversion of bibenzyl to benzene and ethylbenzene along with small amounts of toluene and indan.

3.3.1.2 Hydrogenation of Pyrene

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 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 catalyst was generated by heating titanium 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 oxotitanate in tetralin. Cobalt acac and aluminum isopropylate were used for the preparation of cobalt oxoaluminate. The cobalt oxoaluminate gave a purple solution in tetralin.

A series of reactions was carried out with the iron oxotitanate, cobalt oxoaluminate and K-10 supported iron oxoaluminate, in tetralin at 400°C to determine whether catalytic activity exists for aromatic ring reduction. The reactions of pyrene with these catalysts 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.

Table 2

Catalytic Hydrogenation of Pyrene

Reaction Temp. = 400°C, Reaction time = 2 hrs, H_2 = 1000 psig, S = 0.03 g			
Catalyst (wt.%)	Substr. (mmol)	Conv. (%)	Major Products (mmol)
K-10/IOAl (10)	Pyrene (2.52)	71	4,5-Dihydropyrene (0.48) 1,2,3,3_a,4,5-Hexahydropyrene (0.32) 1,2,3,6,7,8-Hexahydropyrene (0.23) 4,5,9,10-Tetrahydropyrene (0.10) Decahydropyrenes (0.20) (3-isomers) Hexadecahydropyrenes (0.10)
IOTi (10)	Pyrene (2.48)	80	4,5-Dihydropyrene (0.51) 1,2,3,3_a,4,5-Hexahydropyrene (0.42) 1,2,3,6,7,8-Hexahydropyrene (0.28) 4,5,9,10-Tetrahydropyrene (0.10) 1,2,3,3_a,4,5,9,10_a,10_b-Decahydropyrene (0.1) c-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene(0.1) t-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene(0.1) Hexadeacahydropyrene (0.07)
CoOAl (10)	Pyrene (2.52)	67	4,5-Dihydropyrene (0.57) 1,2,3,3_a,4,5-Hexahydropyrene (0.35) 1,2,3,6,7,8-Hexahydropyrene (0.27) 4,5,9,10-Tetrahydropyrene (0.10) Decahydropyrenes (3-isomers) (0.10)

IOTi = Iron oxoatitanate solution in tetralin.
CoOAl = Cobalt oxoaluminate solution in tetralin

In previous work in this project, the reaction of pyrene with iron oxoaluminate tetraisopropoxide gave 67% conversion of pyrene to hydropyrenes (7). For comparison, the thermal reaction of pyrene gave very poor conversion (6%) to dihydropyrene. When the pyrene hydrogenation reaction was carried out using in situ sulfided K-10-supported iron oxoaluminate, a significant improvement in the conversion of pyrene to hydropyrenes was found (71%). Significantly higher amounts of deca- and hexadecahydropyrenes were formed (Table-2). The increase in hydrogenation activity for the clay-supported iron oxoaluminate could be attributed to the formation of a more highly dispersed pyrrhotite on the support surface that does not sinter during the reaction. Although supporting the iron oxoaluminate on the montmorillonite gives a more effective hydrogenation, the hydrocracking activity was decreased somewhat (section 3.3.1.1), perhaps because some of the acidic sites are blocked.

Iron oxotitanate hexaisopropoxide was prepared in tetralin, and a hydrogenation test reaction with pyrene with a small amount of sulfur gave a very high conversion of pyrene (80%). Major products were di-, tetra- and hexahydropyrenes along with a small amounts of decahydropyrenes (3-isomers) and hexadecahydropyrenes. This catalyst gave relatively higher amounts of deca- and hexadecahydropyrenes. These results indicate that catalyst formed by sulfiding the iron oxotitanate is a better hydrogenation catalyst than that from iron oxoaluminate. The higher hydrogenation activity may be due to the higher degree of dispersion obtained with the iron oxotitanate, although a catalyst/support interaction of pyrrhotite with the TiO_2 may have occurred to give a more active catalyst site. The catalyst recovered from this reaction was recycled to determine the loss of activity during hydrotreatment.

Reaction of pyrene with cobalt oxoaluminate tetraisopropoxide and small amount of sulfur gave almost identical conversion and product distribution as that obtained with iron oxoaluminate. It is expected that the molybdenum oxoaluminate and oxotitanate will be highly reactive.

3.3.2 Catalytic Liquefaction of Wyodak

Iron oxoaluminate showed considerable hydrogenation and liquefaction activity for pyrene and Wyodak coal respectively (7). Iron oxotitanate also showed considerable hydrogenation activity for pyrene (3.3.1.2). Like iron oxoaluminate, iron oxotitanate is also soluble in tetralin, and thus can be used as a homogeneous catalyst precursor for liquefaction of coals or first-stage liquefaction products. As-received Wyodak subbituminous coal was heated in tetralin (coal/solvent = 0.5) with and without iron oxotitanate 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. A series of tests with acid-washed Wyodak (IEW) in tetralin (coal/solvent = 0.50) with in situ sulfided supported iron catalysts were also conducted under above conditions. The reaction conditions and conversion data are given in table-3.

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 ARW with iron oxotitanate with sulfur added gave only 8% higher conversion (97%) to THF-soluble products than thermal reaction. The most significant improvement for the in situ sulfided iron oxotitanate catalyst was the increase in the oil fraction (67%). These data is consistent with that observed hydrogenation activity of this catalyst for model compound reaction (Table-2). Compared with iron oxoaluminate, iron oxotitanate gave better overall conversion as well as conversion to heptane-solubles (oils).

Thermal reaction of ion-exchanged Wyodak (IEW) was also conducted under the above conditions. Thermal reaction of IEW gave somewhat lower conversion (86%) than as-received Wyodak. Conversion to heptane-insolubles and heptane-solubles was also slightly lower (Table-3). However, catalytic liquefaction of IEW with iron impregnated K-10 gave significantly higher conversions to THF-solubles as well as heptane-insolubles as well as heptane-soluble products. Reaction of IEW with triiron-impregnated K-10 gave 92% THF-soluble products, 35% being heptane-insolubles and 57% heptane-solubles (oils). Iron hydroxyoxide supported K-10 gave even higher conversion to THF-solubles (95%), with 26% being heptane-insolubles and 69% heptane-solubles (oils). The difference in the reactivity of these two catalysts may be due to the fine particle size of iron hydroxyoxide.

Table 3

Catalytic Liquefaction of Coals

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)	IOTi (15)	Tetralin (10)	97	30	67
IEW (5.23)	None	Tetralin (14)	86	40	47
IEW (5.41)	K-10/Fe_3 (10)	Tetralin (14)	92	35	57
IEW (5.4)	K-10/FeOOH (10)	Tetralin (14)	95	26	69

IOTi = Iron oxotitanate

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