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FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

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by

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1.0 EXECUTIVE SUMMARY

High hydrocracking and liquefaction activity can be achieved with 10 wt.% of sulfided clay-supported iron catalysts. Further tests and demonstrations of this activity were required. Iron hydroxyoxide was generated on acid-treated montmorillonite. The new batch of catalyst exhibited high hydrocracking activity. Three hour tests with the solubilized intermediate from low-severity treatment of Wyodak coal (LSW) gave a high conversion (45%) of the heptane-insoluble LSW intermediate to heptane-soluble products. By comparison, the AMOCAT cobalt-molybdenum catalyst gave 51% conversion to heptane-soluble products. In previous tests with as-received and ion-exchanged Wyodak coal, a similar catalytic effect on conversion to heptane solubles was demonstrated by both catalysts. Thus the more sensitive test with the LSW intermediate shows that the cobalt-moly catalyst may be better at finishing off the hydrogenation that the supported iron catalyst.

An investigation of new methods for the production of catalysts from tetralin-soluble iron oxometallates and the determination of their catalytic activities was continued in this quarter. Iron oxotitanate and iron oxoaluminate gave very high conversions of LSW to heptane solubles (61% and 54%, respectively). These results are consistent with earlier results indicating that the hydrogenation activity of iron oxotitanate was superior to iron oxoaluminate. We presume that very small iron sulfide particles are formed during heating with sulfur, and agglomeration or sintering is prevented by the matrix of titania and alumina in the complexes. When the catalysts were recovered from the reactions and retested with LSW, conversions to heptane-solubles changed to 52% and 55% for the oxotitanate- and oxoaluminate-derived catalysts, respectively, the lower value. The high yields of heptane soluble products obtained with these catalysts offers a potential for use in liquefaction stages with solubilized coal, or at least serve as a model for producing active catalysts via mixed metal oxides.

Methods for successfully testing dispersed iron catalysts with the low-severity intermediate were also devised. Catalyst recovered from the dispersed iron hydroxyoxide-catalyzed reaction of ion-exchanged Wyodak gave a high conversion (47%) of LSW to heptane solubles.

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 be controlled and made larger than those of the zeolites, and hence are more suitable for the adsorption of 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 tenth quarter continued preparation and testing of acid treated montmorillonite clays containing iron in the supported form. Catalytic depolymerization activities of an iron-impregnated clay and a commercial cobalt-molybdenum catalyst were measured in tests with a solubilized low-severity intermediate. Fine particle iron oxides were also prepared and tested for comparisons with the clay-supported catalysts. Liquefaction activity of iron oxotitanate and iron oxoaluminate homogeneous catalyst precursors were determined and compared with activities of the recovered forms of these catalysts.

3.2 Experimental

3.2.1 Catalyst Preparation

3.2.1.1 Preparation of Iron Oxometallates

Iron oxoaluminate and iron oxotitanate were prepared according to the procedure reported earlier (2). Iron oxoaluminate was also prepared in n-decane solvent using the same general procedure (2).

3.2.1.2 Preparation of Supported Catalysts

Procedure for the preparation of Iron hydroxyoxide supported on acid treated montmorillonite (K-10FeOOH) has been described elsewhere (3).

3.2.1.3 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. Co-moly (AMOCAT) was sulfided by heating in a mixture of H_2S and H_2 .

3.2.2 Preparation of Iron Hydroxyoxide-Impregnated Ion-Exchanged Wyodak

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.

Iron hydroxyoxide was supported on ion-exchanged wyodak (IEW) according to the following procedure: Ion-exchanged Wyodak obtained from above was reslurried in 100 ml deionized water and stirred for 30 minutes. A solution of iron (III)

nitrate nonahydrate (0.25 g) in 10 ml deionized water was added to the slurry dropwise with vigorous stirring. After the addition of the iron nitrate, the slurry was stirred for 30 minutes. A solution of 5 g ammonium hydroxide in 50 ml deionized water was added to the slurry dropwise with vigorous stirring. After the addition of ammonium hydroxide, the slurry was stirred for 30 minutes. The product coal was separated by centrifugation, washed with deionized water, and dried in vacuum at 50°C overnight.

Ash contents of the Iron hydroxyoxide impregnated 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). The microreactor 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 Wyodak Coal

A slurry consisting of 5.63 g of coal (iron hydroxyoxide impregnated ion-exchanged Wyodak), 2 wt% of elemental sulfur for in situ sulfidation of catalyst and 14 g tetralin were placed in a 70-ml Parr reactor. 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 Liquefaction of Low-Severity Wyodak Product

A slurry consisting of 1 g low-severity product, 10 wt% desired catalyst, 2 wt% elemental sulfur for in situ sulfidation of iron catalyst, and 2 g tetralin

were placed in a 15 ml microreactor. For the reaction of LSW with iron oxotitanate, a 2 g solution of iron oxotitanate in tetralin was used. The microreactor was pressurized with 1000 psi (initial) of hydrogen. The reactor was placed in a rocking heater heated to 425°C. After the desired temperature was attained, the heating was continued for one hour. At the end of the heating, the reactor was cooled to room temperature and degassed. The contents of the reactor was washed into a centrifugation flask with THF. The THF-extract was centrifuged to remove the insolubles. The THF-insoluble product was washed with THF and dried at 110°C. The THF-soluble product was evaporated to remove THF. The product obtained after evaporation of THF was added to a large excess of n-heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane and dried in vacuum at 50°C. The heptane-insoluble product was determined by difference.

3.2.6 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

A fresh batch of supported catalyst was prepared by supporting iron hydroxyoxide on acid-treated montmorillonite (K-10). Hydrocracking activities of this catalysts was investigated by heating bibenzyl (0.5 g, 2.75 mmol) and catalyst along with a small amount of sulfur (for in situ sulfidation) for 3 hours at 350°C in the presence of 1000 psi of H₂ (cold).

Reaction of bibenzyl with 10 wt% of the catalyst 64% conversion of the bibenzyl to lighter products. Major product were benzene (1.20 mmol) and ethylbenzene (0.50 mmol) along with small amount of toluene (0.12), indan (0.02 mmol) and tetralin (0.03 mmol). No coke or oligomeric products were formed indicating the absence of retrograde condensation reaction. These results are similar to those obtained with earlier batch of the same catalyst.

3.3.2 Catalytic Liquefaction of Wyodak

The results of liquefaction of as-received Wyodak subbituminous coal (ARW) and ion-exchanged Wyodak coal (IEW) with iron-impregnated and iron-pillared catalysts were reported in previous quarterly reports and compared with results from iron hydroxyoxide formation on the as-received coal. A second trial with the iron hydroxyoxide prepared on the ion-exchanged Wyodak coal was desired to check the reproducibility of the reaction. The liquefaction of iron hydroxyoxide-impregnated ion-exchanged Wyodak was carried out by heating the coal in tetralin (coal/solvent = 0.5) 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-1.

Table 1
Catalytic Liquefaction of Wyodak Coal

Reaction Temp = 425°C, Reaction Time = 1 hr, Sulfur (wt%) = 2 H ₂ = 1000 psi (cold)					
Coal	Catalyst (wt.%)	Solvent (g)	Conversion (%)	Heptane-I (%)	Heptane-S (%)
ARW	None	Tetralin (14)	89	41	48
IEW	None	Tetralin (14)	86	40	47
ARW	FeOOH	Tetralin (14)	88	36	52
IEW (Rxn 1)	FeOOH	Tetralin (14)	91	36	56
IEW (Rxn 2)	FeOOH	Tetralin (14)	96	41	55

The uncatalyzed (thermal) reaction of ARW coal gave 89% conversion of coal to THF-soluble products, with 48% being heptane-soluble products. The thermal reaction of IEW gave somewhat lower conversion (86%) than as-received Wyodak. The reaction of iron hydroxyoxide-impregnated coal gave 96% conversion of the coal to THF-soluble products. This result compares with 91% obtained for the same reaction at an earlier time. The deviation may be due to the small amounts of material which must be weighed when the conversions are this high, as well as the difficulty in removing water and the polar solvents from this fraction. Since high conversions to THF-solubles are easily obtained at 400°C without any catalyst with the low-rank coals, large deviation in values is not of great consequence. The second reaction of IEW with sulfided impregnated iron hydroxyoxide catalyst showed 55% conversion to heptane solubles, essentially the same as in the earlier reaction. It is likely that the conversion to oils and asphaltenes is more precisely determined than the conversion to THF solubles and provides a better evaluation of the activity of the catalysts.

3.3.3 Liquefaction of Low-Severity Products

In an earlier report (4) we described the use of a mineral-free solubilized intermediate from low-severity CO/H₂O/tetralin treatment of Wyodak coal for testing catalysts for depolymerization activity. The conversion of the THF-soluble, heptane-insoluble fraction to heptane solubles was measured. These

tests showed a large degree of catalytic effect for a sulfided iron/alumina-pillared clay in a one hour test (30% conversion versus 15% in the thermal reaction). Furthermore, in a three hour test, the iron/alumina-pillared catalyst showed a 42% conversion of heptane insolubles to heptane solubles. Additional testing at three hours was desired for the iron-impregnated clay catalysts prepared later in the project, as well as the commercial cobalt-molybdenum catalyst. The reaction was carried out by heating 1 g of the LSW and 2 g tetralin with 10 wt% of the catalyst and 2 wt% of elemental sulfur (in situ sulfidation) at 425°C for 3 hours in 1000 psi of initial hydrogen pressure. These results for the three hour tests with LSW are reported in Table 2.

The reaction of LSW with iron hydroxyoxide supported on acid-treated clay (I-Mont) gave 45% conversion to heptane-soluble oil product. In comparison, the AMOCAT Co-Moly catalyst gave 51% conversion of to heptane-soluble oils. In previous tests with as-received or ion-exchanged Wyodak coal, a similar catalytic effect on the heptane-soluble yield was demonstrated by both catalysts. It appears that the cobalt-moly catalyst may be better at finishing off hydrogenation of the coal macromolecules, and this effect does show up in the more sensitive LSW test.

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

Iron oxotitanate hexaisopropoxide and iron oxoaluminate tetraisopropoxide were generated by heating titanium isopropoxide or aluminum isopropoxide and ferrous acetate in tetralin in a stream of dry nitrogen. Distillation of isopropyl acetate formed during reaction gave a green solution of iron oxoaluminate in tetralin. Iron oxotitanate was a reddish solution in tetralin. Iron oxoaluminate and iron oxotitanate showed considerable hydrogenation and liquefaction activity for pyrene and Wyodak coal respectively (7). Both iron oxoaluminate and iron oxotitanate can be used as a homogeneous precursor for coal liquefaction catalysts.

To test the depolymerizing activity of the sulfided catalysts formed from these soluble precursors, low-severity product (THF-soluble, heptane insoluble) obtained from the liquefaction of Wyodak subbituminous coal was catalytically treated as described above. The reaction was carried out by heating 1 g of the LSW and 2 g tetralin with 10 wt% of the catalyst precursor and 2 wt% of elemental sulfur (in situ sulfidation) at 425°C for 3 hours in 1000 psi of initial hydrogen pressure. The conversion data are given in Table-2.

TABLE 2

Catalytic Hydrotreatment of Low-Severity Wyodak Product

LSW = 1 g, Tetralin = 2 g, Sulfur = 2 wt%, H ₂ = 1000 psi(cold) Reaction Temp. = 425°C, Reaction Time = 3 hrs.		
Catalyst (wt%)	Heptane-I (%)	Conv. to Heptane-S (%)
K-10/FeOOH (10)	55	45
Co-Moly (10)	49	51
IOTi (10)	39	61
IOTi (recov.) (10)	48	52
IOAl (10)	46	54
IOAl (recov.) (10)	45	55
FeOOH (recov.)*	53	47

* = FeOOH was recovered as a mixture of coal ash and THF-insoluble material from the liquefaction of FeOOH-impregnated ion exchanged Wyodak coal (Table 1).

The reaction of LSW with sulfided iron oxotitanate-derived catalyst gave a significantly higher conversion (61%) of heptane insolubles to heptane solubles than the heterogeneous iron or cobalt-moly catalysts described above. A major factor in the higher activity may have been the extremely small size of the initial catalyst particles. A determination of the catalytic activity of the sulfided iron titania catalyst recovered from the reaction was carried out in a second test with LSW. The conversion in the test with recovered catalyst was lower (52%). The lower activity may have resulted from agglomeration during cooling or collection (centrifugation) or drying.

Sulfided iron oxoaluminate was also tested with LSW. This catalyst gave 54% conversion to oils in the initial test and 55% conversion in the test with recovered catalyst. Further work is needed to characterize the particle size of both the oxoaluminate and oxotitanate-derived catalysts. Both catalysts show promise for a liquefaction stage employing a highly dispersed catalyst with a low severity solubilized coal intermediate.

For comparison purposes, we also wished to determine the activity of sulfided fine iron hydroxyoxide catalyst (PETC preparation method) in the LSW

test. The preparation of the fine iron hydroxyoxide catalyst for liquefaction of the low-severity product involved recovering the THF-insoluble fraction from the liquefaction of iron hydroxyoxide-impregnated (PETC method) ion-exchanged Wyodak coal. The entire THF-insoluble fraction was used as the catalyst for the depolymerization of LSW. This THF-insoluble product is a mixture of iron hydroxyoxide, residual coal ash and unconverted coal. This catalyst gave 47% conversion of heptane-insolubles to oils. This conversion is comparable with that observed for the iron-impregnated clay catalyst (45% conversion).

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