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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 of mixed pillared clay catalysts and clay-supported catalysts and determination of their catalytic activities were continued in this quarter. To demonstrate the reproducibility of the preparative method for high activity iron/alumina-pillared montmorillonite catalysts, a new batch of the catalyst was prepared and tested for hydrocracking activity with bibenzyl. This preparation gave conversion and product distribution similar to that reported previously, demonstrating that the preparative technique we have developed results in identical catalysts. A 50 wt.% concentration of the catalyst gave only slightly higher conversion (86%) than the 10 wt% concentration (84% conversion), indicating that small amounts of the high activity catalyst are sufficient for hydrocracking.

The mixed iron/alumina-pillared clay was also prepared using a pillaring solution that was aged for longer period of time. The catalyst prepared from the two week-aged alumina pillaring solution exhibited lower hydrocracking activity than that prepared from the 3 day-aged solution.

To determine the importance of the type of pillaring support in hydrocracking activity, iron/zirconia-pillared montmorillonite was prepared using the same technique as that for iron/alumina-pillared montmorillonite. The reaction of bibenzyl with the sulfided iron/zirconia-pillared catalyst gave a lower hydrocracking conversion than the iron/alumina-pillared catalyst. The iron/zirconia-pillared clay was washed with 0.1 M ammonium nitrate solution in order to remove any residual Na^+ ions from the catalyst. However, this procedure gave a catalyst that was relatively inactive for hydrocracking.

Farcasiu and others showed that sulfated iron catalysts were effective for hydrocracking. By stabilizing sulfated iron on an a clay support, the resistance to sintering and consequently the activity of this type of catalyst might be improved. However, previous work in this project showed that catalysts prepared by adding ferric sulfate and ammonia or ferric sulfate and urea to an acid-washed clay gave poor catalysts. Since hydration or rehumidification of the catalyst may be necessary for activation of the acidic sites, addition of 10 wt% water to the reaction was attempted. This procedure only marginally improved the conversion. These catalysts were then saturated with water by passing moist argon vapors through the catalysts for several hours. Testing of these catalysts with a model compound showed that their hydrocracking activity was considerably higher than dry catalysts.

Addition of a second catalytic metal to the clay support was attempted to determine if a synergistic effect could improve liquefaction. Ferric nitrate and stannous chloride were added to the clay, but the resulting catalyst was relatively poor for hydrocracking and hydrogenation compared with ferric nitrate supported on the clay.

New disposable iron catalysts with high acidity and surface area are desired for coal liquefaction. Synthetic iron aluminosilicates were prepared by methods similar to those used for the nickel-substituted synthetic mica montmorillonite (NiSMM) catalysts, which are very effective for hydrogenation and reforming of hydrocarbons. The iron aluminosilicate catalysts were prepared from both ferric nitrate and ferrous acetate and were tested for hydrocracking and hydrogenation of bibenzyl, naphthalene and pyrene. The hydrocracking activity of the unsulfided iron aluminosilicates was lower than that exhibited by the NiSMM catalyst. However, sulfidation of an iron aluminosilicate resulted in significant improvement in the hydrocracking activity of the catalysts. Similarly sulfidation of the synthetic iron catalyst is essential for hydrogenation of naphthalene and pyrene. Pyrene hydrogenation was effectively catalyzed by the sulfided synthetic iron catalyst. Further work is needed to characterize the new catalyst and understand the structure/activity relationships.

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.

Synthetic clays have been reported to be more active catalysts than natural clays (2-4). Synthetic mica montmorillonite (SMM) containing a hydrogenation component could be used for hydrocracking processes (5,6). The incorporation of cobalt and, especially, nickel into the SMM structure dramatically improves the hydrocracking and hydroisomerization of light straight chain paraffins (7,8). Exactly how the incorporation of nickel or cobalt enhanced the activity is unknown (9). Nickel-substituted synthetic mica montmorillonite has been found to be a good hydrocracking and hydrogenation catalyst for coal liquefaction (10).

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 sixth quarter continued preparation and testing of pillared clays and non-pillared clays containing iron in the supported as well as intercalated forms.

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. (12). The detailed procedure has been described in a previous quarterly report (11).

3.2.1.2 Preparation of Pillared Clay Catalysts

Alumina-pillared montmorillonite and zirconia-pillared montmorillonite were prepared and intercalated with trinuclear acetato-hydroxo iron(III) nitrate. Detailed procedures have been described in our previous reports (13-16). Pillaring solution obtained from the hydrolysis of aluminum chloride with sodium hydroxide aged several days was also used for the preparation of alumina-pillared montmorillonite. Triiron-intercalated zirconia-pillared montmorillonite was also washed with 0.1 N ammonium nitrate prior to calcination.

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. Preparation of mixed metals supported on K-10 using a solution of stannous chloride dihydrate and triiron heptaacetato nitrate has been described in our previous report (16). Preparation of ferric sulfate treated K-10 using NH_4OH ($K\text{-}10Fe_2(SO_4)_3/NH_4OH$) and urea ($K\text{-}10Fe_2(SO_4)_3$/Urea) has also been described in our previous quarterly report (16).

For the activation of ferric sulfate treated K-10, 0.50 g of the catalyst was placed in a glass tube and supported with glass wool plugs. The glass table was attached to a bubbler containing water. The bubbler was attached to Argon tank, and argon saturated with water was passed through catalysts for 3 hours. The humidified catalyst was kept for testing.

3.2.1.4 Preparation of Iron Aluminosilicate Catalyst

An iron aluminosilicate catalyst (FEAS) was prepared by the procedure that Heinerman (17) reported for the preparation of nickel-substituted synthetic mica montmorillonite. A sodium silicate solution, 14.0 g (27 wt.% SiO_2), was dispersed in 150 ml of deionized water. The sodium silicate solution was exchanged three times with Amberlite IR 120-H cation resin. Next, 10 g of iron(II) acetate dissolved in 50 mL water was added with stirring to the silica dispersion. Then 9.4 g of aluminum isopropoxide and 0.3 g of ammonium fluoride were added with stirring. The resulting slurry was evaporated to remove some water until the volume was about 100 ml. Two milliliters of aqueous ammonia (25% NH_3) was then added, and the slurry was transferred to a glass container in a 300-mL stainless steel pressure vessel without a stirring device. The temperature was slowly raised to 300°C and kept at this level for 40 hours. Then the pressure vessel was cooled to room temperature. The product was separated by centrifugation and washing with deionized water, and dried at 120°C for 16 hours. The dried material was ground to -100 mesh and calcined in air at 540°C for 6 hours. The calcined FEAS was stored in air tight bottles for further use.

A second batch of FEAS was prepared by a similar procedure, except that iron(II) nitrate was used in the preparation instead of iron(II) acetate. This product was named FEAS-N.

3.2.1.5 Sulfidation of Catalysts

All the catalysts used in these investigations were in situ sulfided. A small amount of carbon disulfide or 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.

3.2.3 Catalytic Hydrotreating of Model Compounds

In a typical run, 0.50 g of the test compound, appropriate amount of the desired catalyst and equivalent amounts of carbon disulfide or elemental sulfur (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.

3.3 Results and Discussion

3.3.1 Clay-Supported Sulfated Iron Catalysts

Catalytic Hydrocracking Tests with Rehumidified Catalysts

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 (18), 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 (14). Also, previous results with iron-pillared clays demonstrated that in situ sulfidation of the catalyst with a small amount of carbon disulfide produced hydrocracking activities somewhat better than those obtained by presulfidation with H_2 and H_2S (14).

Ferric sulfate is another iron precursor which is used for coal liquefaction catalysts. Ferric sulfate is converted to a colloidal iron oxide form by hydrolysis with urea. This procedure leaves some of the iron in a sulfated form which can form strong Bronsted acid sites. The potential exists for a clay support interaction with the sulfated iron that will stabilize the colloidal form and keep it from sintering or agglomerating. Thus, a mixture of ferric sulfate and urea was added to acid-treated K-10 clay. The catalyst obtained after calcination was tested for hydrocracking of bibenzyl during previous quarter. Reactions of bibenzyl with 10 wt% of this catalyst gave poor conversions of bibenzyl (16). The reaction of ferric sulfate supported on K-10 clay and washed with ammonium hydroxide also gave very poor conversion (5%) of bibenzyl into products (16).

Farcasiu and coworkers reported that the addition of a small amount of water to the sulfated iron catalysts (rehumidification) significantly improved coal conversion during coal liquefaction (19). In order to determine the effect of adding water to the clay-supported catalyst to increase hydrocracking activity, the catalyst prepared by addition of iron(III) sulfate to a commercial acid-treated clay (K-10), followed by ammonium hydroxide treatment, was tested both by adding water to the reaction mixture and by rehydrating the catalyst in a water saturated gas stream as reported by Farcasiu (19). The catalyst was sulfided in-situ with elemental sulfur to convert the iron to active pyrrhotite.

The reaction of bibenzyl with 10 wt.% of the catalyst prepared by ammonia-catalyzed hydrolysis of ferric sulfate supported on K-10 (K-10/$Fe_2(SO_4)_3$/NH_4OH) and 10 wt.% added water was carried out at 350°C for 3 hours in the presence of 1000 psig of initial hydrogen pressure. Reaction conditions, conversion data, and major products are given in Table 1. The reaction of bibenzyl in the reaction with added water gave 12% conversion, which is only slightly higher than the 5% conversion obtained in the absence of water (Table 1).

Table 1

CATALYTIC ACTIVITY OF CLAY-SUPPORTED SULFATED IRON CATALYSTS

Reaction Temp. = 350°C, Sulfur, H_2 = 1000 psig

Catalyst (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
K-10$Fe_2(SO_4)_3/NH_4OH$ (10) "Dry"	2.74	5	Benzene (0.11) Toluene (0.01) Ethylbenzene (trace)
K-10$Fe_2(SO_4)_3/NH_4OH$ (10) Water (10)	2.80	12	Benzene (0.07) Toluene (0.20) Ethylbenzene (trace)
K-10$Fe_2(SO_4)_3/NH_4OH^*$ (10) "Rehumidified"	2.75	33	Benzene (0.42) Toluene (0.11) Ethylbenzene (0.10)
K-10$Fe_2(SO_4)_3$/Urea (10) "Dry"	2.72	14	Benzene (0.20) Toluene (0.18) Ethylbenzene (0.08)
K-10$Fe_2(SO_4)_3$/Urea* (10) "Rehumidified"	2.75	61	Benzene (1.20) Toluene (0.04) Ethylbenzene (0.29)

* = catalysts rehumidified by passing vapors of argon saturated with water.

When the same catalyst was humidified by passing water-saturated argon vapors through the catalyst, the conversion of bibenzyl was significantly higher (33%) than with the dry catalyst (5%). Similarly, the catalyst prepared by urea hydrolysis of ferric sulfate supported on K-10 (K-10/$Fe_2(SO_4)_3$/urea) was humidified by passing water-saturated argon. This catalyst gave a significantly higher conversion (60% vs 14% for dry catalyst) of bibenzyl into low molecular weight products.

High resolution GC analysis indicated similar product distributions for all these reactions (Table 1). The major products were benzene, toluene, and ethylbenzene. Benzene and ethylbenzene were formed in the largest amounts, and the ratio of benzene to ethylbenzene was 2-4, indicating the occurrence of further cracking of the ethylbenzene to benzene. The formation of these products is indicative of the Bronsted acid catalysis mechanism (14). The increase in the activity may be attributed to association of water with sulfated iron sites so as to formed strong Bronsted acid sites.

3.3.2 Hydrogenation Activity of Clay-Supported Iron/Tin Catalysts

Tin has also been found to be effective for coal liquefaction. On heating in hydrogen, tin (II) was converted into an elemental form, which effectively transferred hydrogen to coal fragments or model compounds (20). Synergism between iron and tin has been reported for coal liquefaction (21). In order to investigate this phenomenon further, a mixture of stannous chloride and triiron complex were dissolved in ethanol, supported on K-10 using an incipient wetness method, and calcined. The reaction of bibenzyl gave 39% conversion of bibenzyl into mainly benzene, toluene and ethylbenzene (16), which was lower that obtained with other clay-supported iron catalysts. In this quarter the hydrogenation activity of the supported mixed metal catalyst was investigated. Pyrene was hydrogenated with 10 wt% of K-10 clay-supported iron/tin catalyst at 350°C for 3 hours. Only 30 % of the pyrene was hydrogenated (Table 2). Compared with triiron supported on K-10, the mixed metal supported clay is a poor hydrogenation catalyst.

Table 2

HYDROGENATION ACTIVITY OF CLAY-SUPPORTED IRON/TIN CATALYSTS

Reaction Temp. = 350°C, Reaction Time = 3 hrs, Pyrene = 2.52, Sulfur = 0.03 g, H_2 = 1000 psig		
Catalysts (wt%)	Conversion (%)	Major Products (mmol)
K-10Fe_3Sn^{2+} (10)	30	Decahydropyrenes (3-isomers (trace) 1,2,3,3_a,4,5-Hexahydropyrene (0.04) 1,2,3,6,7,8-Hexahydropyrene (0.05) 4,5,9,10-Tetrahydropyrene (0.07) 4,5-Dihydropyrene (0.47)

3.3.3 Synthetic Iron Aluminosilicate Catalysts

An iron aluminosilicate (FEAS) catalyst was prepared by a methods similar to that used to make nickel-substituted synthetic mica montmorillonite, by using iron(II) salts instead of nickel. The FEAS catalysts were prepared from both iron (II) acetate as well as iron(III) nitrate (FEAS-N), to determine the effect of iron precursor on the hydrocracking and hydrogenation activities of the catalyst. The catalysts were tested for hydrocracking and hydrogenation activities with bibenzyl, naphthalene and pyrene as the substrates. The analytical data are presented in Table 3.

3.3.3.1 Catalytic Hydrocracking of Bibenzyl

The reactions of bibenzyl were carried out at 350°C for 3 hours in the presence of 1000 psig initial pressure of molecular hydrogen (Table 3). In separate tests, FEAS catalysts were sulfided in situ by adding a small amount of sulfur before hydrotreating. The reaction of bibenzyl with sulfided FEAS prepared from iron(II) acetate (FEAS-1) gave 53 % conversion of bibenzyl. Major products were into benzene and toluene. To determine the effect of age of aluminum isopropoxide on the catalytic activity of the resulting FEAS catalyst, a reaction using a (sulfided) FEAS prepared from iron(II) acetate but using a fresh prepared solution of aluminum isopropoxide (FEAS-2) gave a similar conversion (50%). Somewhat more benzene and ethylbenzene were formed in this case.

Table 3

HYDROCRACKING ACTIVITY OF SYNTHETIC IRON ALUMINOSILICATE CATALYSTS

Reaction Temp. = 350°C, Reaction Time = 3 hrs, H_2 = 1000 psig				
Catalyst (wt.%)	Bibenzyl (mmol)	Sulfur (g)	Conversion (%)	Major Products (mmol)
FEAS-N (10)	2.80	None	10	Benzene (0.10) Toluene (0.05)
FEAS-N (10)	2.75	0.03	53	Benzene (1.04) Toluene (0.07) Ethylbenzene (0.16) Indan (0.03) Tetralin (0.04)
FEAS-1 (50)	(2.75)	None	24	Benzene (0.42) Toluene (0.03) Ethylbenzene (0.11)
FEAS-1 (10)	(2.75)	0.03	53	Benzene (1.06) Toluene (0.24) Ethylbenzene (0.14) Indan (0.02) Tetralin (0.03)
FEAS-2 (10)	(2.80)	None	21	Benzene (0.38) Toluene (trace) Ethylbenzene (0.10)
FEAS-2 (10)	(2.75)	0.03	50	Benzene (1.11) Toluene (0.17) Ethylbenzene (0.20) Indan (0.02) Tetralin (0.03)

a = FEAS-N prepared from iron(III) nitrate.
b = FEAS-1 prepared from iron(II) acetate.
c = FEAS-2 prepared from iron(II) acetate with fresh aluminum isopropoxide.

The reaction with the iron aluminosilicate prepared from iron (III) nitrate also gave a similar conversion (53%) and product distribution. Formation of these products is indicative of a carbonium ion mechanism catalyzed by Bronsted acid sites (10). Formation of toluene may have been Lewis acid catalyzed. In addition to these products, a very large number of other products in much smaller concentrations were also observed. These products may have been formed from the hydrogenation, hydroisomerization, or ring opening reactions. No oligomeric material or coke were formed.

Reactions with the unsulfided FEAS-1, FEAS-2, and FEAS-N catalysts gave 24, 21, and 10% conversions, respectively. These data indicate that sulfiding the iron in the synthetic aluminosilicate catalyst is essential for high catalytic activity. Conversion of some of the iron to perhaps form micropyrhhotite sites that can activate or transfer hydrogen for reduction of intermediate carbonium ions, preventing condensation and coking and thereby maintaining catalyst activity. More work is needed to fully understand the effect of sulfidation on the hydrocracking activity of these catalysts.

3.3.3.2 Catalytic Hydrogenation of Naphthalene

The hydrogenation activity of sulfided iron aluminosilicate FEAS-N was investigated by hydrogenating naphthalene at 350°C for 3 hours in the presence of 1000 psi of initial hydrogen pressure. Reactions were carried out by using 10 and 20 wt.% of the catalysts. Reaction of naphthalene with 10 wt.% of FEAS-N gave only 8% conversion of naphthalene to tetralin. Similar reaction using 20 wt.% of the catalyst gave significantly higher conversion (48%) of naphthalene to tetralin. A small amount of decalin was also formed. In addition to hydronaphthalenes, 11 wt% of alkylbenzenes were formed from the hydrocracking of naphthalene.

Table 4

CATALYTIC HYDROTREATING OF NAPHTHALENE

Reaction Time = 3 hrs, Reaction Temp. = 350°C, H_2 = 1000 psig			
Catalyst (wt.%)	Naphthalene (mmol)	Conversion (%)	Major Products (mmol)
FEAS-N (10)	3.91	8	Tetralin (0.30) Decalin (trace)
FEAS-N (20)	3.91	48	Tetralin (1.42) Decalin (0.02) Cracked Product (11%)

3.3.3.3 Catalytic Hydrotreating of Pyrene

Catalytic hydrotreating of pyrene was investigated to determine the activity of the sulfided iron aluminosilicate catalysts for hydrogenation and hydrocracking of polynuclear aromatic systems common to most coals. Previous results have shown that in situ sulfided NiSMM using 50 wt% loading is an effective hydrogenation catalyst for pyrene. However, the hydrocracking activity was low under these conditions. The low hydrocracking activity was attributed to the absence of very strong Bronsted acid sites, thus higher temperatures may be needed for pyrene cracking (10). Hydrotreating was carried out with 10 wt% of FEAS-2 at 350°C for 3 hours in the presence of 1000 psi of hydrogen. The reaction conditions, conversion data, and product distributions are given in Table 5.

Table 5

CATALYTIC HYDROTREATING OF PYRENE

Reaction Time = 3 hrs, Reaction Temp. = 350°C, H_2 = 1000 psig, S = 0.03 g, Pyrene = 2.52 mmol		
Catalyst (wt%)	Conversion (%)	Major Products (mmol)
FEAS-2 (10)	82	Hexadecahydropyrene (3 isomers)(0.01) 1,2,3,3_a,4,5,9,10_a,10_b-Decahydropyrene (0.08) c-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene(0.07) t-1,2,3,3_a,4,5,5_a,6,7,8-Decahydropyrene(0.09) 1,2,3,3_a,4,5-Hexahydropyrene (0.24) 1,2,3,6,7,8-Hexahydropyrene(0.36) 4,5,9,10-Tetrahydropyrene (0.13) 4,5-Dihydropyrene (0.43) Cracked Products (24%)

The hydrogenation of pyrene with FEAS-2 gave a high conversion (82%) of pyrene into products. The majority of the products were di-, tetra-, and hexahydropyrenes. Since we did not calibrate for these isomers, data are derived from FID area percent data, assuming the response factors of pyrene and hydropyrenes to be the same. Relatively small amounts of hexadecahydro-, and decahydropyrenes were also formed. Hydrogenation activity was similar to that of NiSMM reported earlier (10). In addition to hydropyrenes, substantial amounts of lower molecular weight components (about 24% 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. Further work is in progress to develop catalysts and conditions suitable for hydrogen transfer as well hydrocracking of polynuclear aromatics.

3.3.43 Mixed Pillared-Montmorillonite Catalysts

Previous results have shown that incorporation of alumina pillars into montmorillonite-supported catalysts prevented the collapse of layer structure upon sulfidation of the iron pillars. The mixed iron/alumina-pillared montmorillonite gave high conversions of bibenzyl into low molecular weight products. The increased activity was attributed to the strong acid sites associated with alumina pillars (14-16). To determine the reproducibility of the preparative technique, a fresh batch of iron/alumina-pillared montmorillonite was prepared by intercalation of oxyaluminum and triiron complex cations into sodium montmorillonite. The iron/alumina-pillared clay catalyst was tested for hydrocracking activity using bibenzyl with 10 or 50 wt.% catalyst concentrations (in situ sulfidation) at 350°C for 3 hours in the presence of 1000 psi of initial hydrogen pressure in a 15 ml rocking autoclave reactor. Conversion data and major products are presented in Table 6.

Reactions of bibenzyl with 10 and 50 wt.% in situ sulfided iron/alumina-pillared montmorillonite (APC-Fe_3) gave 84% and 86% conversions of bibenzyl into products. The conversion and product distribution were similar those obtained with previously prepared catalyst (16). These results indicate that under identical conditions, the preparative technique we have used for the preparation of mixed pillars pillared clay catalysts formed identical catalysts. These reactions also show that 10 wt% of catalyst is sufficient to achieve high hydrocracking activity with pillared clay catalyst.

The major products from the reaction were benzene, toluene and ethylbenzene. The ratio of benzene to ethylbenzene was about 3. Hydrogenation of single-ring aromatics was minimal under these conditions. Small amounts of alkylbenzene products resulted from hydrogenation of bibenzyl followed by cracking reactions, probably involving Lewis acid sites. Higher molecular weight components were insignificant as indicated by GC analysis with a short 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, which further indicate that no retrograde reactions or coke were observed during reactions.

In order to determine the role of type of pillars on the catalytic activity of the mixed pillared clay catalysts, iron/zirconia-pillared montmorillonite was prepared by the same method as that used for the mixed iron/alumina montmorillonite. The reaction of bibenzyl with 10 wt% of in situ sulfided iron/zirconia-pillared clay gave a 67% conversion of bibenzyl into products. Major products were benzene, toluene and ethylbenzene. The ratio of benzene to ethylbenzene was 4. The lower conversion with this catalyst may indicate that zirconia-pillaring creates either fewer or weaker Bronsted acid sites than alumina-pillaring. Further work is needed to prove that this is true. Hydrogenation of polynuclear aromatic compounds might be efficiently carried out with catalyst, and these studies are in progress.

Table 6

CATALYTIC ACTIVITY OF IN SITU-SULFIDED MIXED PILLARED CLAY CATALYSTS

Reaction Temp. = 350°C, Reaction time = 3 hrs, H_2 = 1000 psig, S = 0.03 g

Catalyst (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
APC-Fe_3 (10)	2.80	84	Benzene (1.79) Toluene (0.23) Ethylbenzene (0.57) Indan (0.04) Tetralin (0.07)
APC-Fe_3 (50)	2.75	86	Benzene (2.00) Toluene (0.24) Methylcyclohexane (0.04) Ethylbenzene (0.82) Ethylcyclohexane (0.01) Indan (0.04) Tetralin (0.05)
ZPC-Fe_3 (10)	2.80	67	Benzene (1.28) Toluene (0.11) Ethylbenzene (0.34) Indan (0.04) Tetralin (0.07)

Other preparative techniques, such as ageing of the pillaring solution and washing of the pillared clay catalysts with ammonium nitrate, were investigated for their effects on the catalytic activity of mixed pillared clay catalysts . The oxyaluminum pillaring solution was aged for two weeks prior to intercalation into the sodium montmorillonite. The reaction of bibenzyl with 10 wt% of iron/alumina-pillared catalyst prepared from the aged solution gave 69% conversion. Thus, the conversion and product yields are significantly lower than those obtained with the catalyst prepared by using pillaring solution aged for 72 hours (Table 6). This may indicate that longer ageing of the pillaring solution form polyoxy cations of different stoichiometry and weaker Bronsted sites.

Residual Na^+ ions in the catalyst may result in lower hydrocracking activity. The residual sodium ions could perhaps be removed by washing with ammonium nitrate. Iron/zirconia-pillared catalyst was washed with 0.1 M NH_4NO_3, and then calcined at 350°C for 3 hours. Reaction of bibenzyl with in situ-sulfided ammonium nitrate-washed iron/zirconia-pillared clay gave only 3% conversion. Small amounts of benzene and toluene were the only products. Reasons for the very poor hydrocracking activity are still under investigation. The iron oxide form may have changed significantly as a result of the washing procedure.

Table 7

EFFECTS OF PREPARATIVE TECHNIQUES ON REACTIONS WITH MIXED PILLARED CLAY CATALYSTS

Reaction Temp. = 350°C, Reaction Time = 3 hrs, H_2 = 1000 psig, S = 0.03 g			
Catalyst (%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
APC-Fe_3[a] (10)	2.80	69	Benzene (1.42) Toluene (0.01) Ethylbenzene (0.24) Indan (0.03) Tetralin (0.03)
ZPC-Fe_3[b] (10%)	2.80	3	Benzene (0.02) Toluene (0.10)

a = Pillaring solution was aged for longer period.
b = iron/zirconia-pillared clay was washed with 0.1 N ammonium nitrate prior to calcination.

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