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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 iron-pillared clay catalysts and clay-supported iron hydroxyoxide catalysts and the determination of their catalytic activities was continued in this quarter. New pressure reaction vessels and equipment for gas filling were constructed to provide greater safety ratings.

Previous work in this project showed that a catalyst prepared by adding ferric nitrate and ammonia to an acid-washed clay gave an active catalyst following sulfidation. Further testing of this catalyst with a model compound showed that its hydrocracking activity was considerably lower when used in 10% concentration rather than 50%. The conversion also diminished considerably when a one hour reaction time was used. In contrast, the mixed iron/alumina pillared clay catalysts were still highly effective at 10% concentration and gave good conversions at one and two hour reaction times.

An investigation of preparation methods demonstrated that calcination of both the iron hydroxyoxide-impregnated clay and the mixed iron/alumina pillared clays is essential for activity. High activity was obtained for these catalysts only when they were removed from the aqueous media **rapidly**, dried, and calcined. When the iron-intercalation was carried after calcination of an alumina-pillared clay, a slightly less active catalyst was obtained.

The use of ferric sulfate to prepare a clay-supported sulfated iron catalyst was attempted, the resulting catalyst was relatively inactive for hydrocracking.

Several new catalysts were synthesized with the idea of decreasing the pillar density and thereby increasing the micropore volume. A zirconia-pillared clay with low pillar density was prepared and intercalated with triiron complex. The hydrocracking activity of this catalyst was somewhat lower than that of the mixed alumina/iron-pillared catalyst. Further reactions with larger model substrates are planned so that large pore selectivities can be demonstrated.

Alumina-pillared supports were prepared adding polyvinyl alcohol to complex the polyoxyaluminum cations during the exchange into the clay. These gave poor hydrocracking activities after iron intercalation and sulfidation. Other new catalysts, that were prepared by first pillaring with an organic ammonium pillaring agent, then introducing a lower number of silica or alumina pillars, and finally the iron component, were also tested. One of these was relatively active in hydrocracking tests. Since these contain a carbon residue, other selectivities or uses for the catalyst may exist and further burn-out of the carbon can be attempted.

The mixed alumina/iron-pillared catalysts was further tested at low concentration for pyrene hydrogenating and hydrocracking activities. A high conversion to hydrogenation products was obtained at 350°C, and 17% conversion to cracked products was obtained (no coking). These results compare favorably with those obtained with a Ni-Mo catalyst.

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

3.2.1.2 Preparation of Pillared Clay Catalysts

Preparation of iron-impregnated silica-pillared catalyst from the dodecylammonium montmorillonite precursor (DAM-SP-Fe^{3+}) and triiron-intercalated silica-pillared catalyst from DAM prepared in DMF (DAM-SP-Fe_3-DMF) have been described in the previous quarterly report (4).

Preparation of triiron-intercalated polyvinyl-alumina-pillared montmorillonite (PVA-APC-Fe_3)

Preparation of polyvinyl-alumina-pillared montmorillonite: A solution of 8.78 g of polyvinyl alcohol in 88 ml deionized water was prepared by stirring for 4 hours. To this solution was added 8.78 g of Na-montmorillonite and stirred for 5 minutes. Pillaring solution (350 ml of 0.015M $Al_{13}O_4(OH)_{24}Cl_7$) was added dropwise and stirred for 24 hours. The clay was separated by centrifugation and washing with deionized water. The residue was dried at 110°C and calcined at 500°C for 1 hour. A dark charcoal product was obtained.

Intercalation of pillared clay: Triiron heptaacetato nitrate complex was intercalated into the above clay using the procedure described below for intercalation of zirconia-pillared clay.

Preparation of zirconia-pillared montmorillonite (ZPC)

Preparation of pillaring solution: Zirconyl chloride octahydrate (6.11 g) was dissolved in 1000 ml deionized water, and the pH was adjusted at 1.3 by adding 0.1N NaOH. The resulting cloudy solution was stirred for 10 days while maintaining the pH at 1.3.

Pillaring reaction: Na-montmorillonite (1 g) was added to 100 ml water and stirred for 4 days. The pH was adjusted at 9.1 by adding 0.1N NaOH. To the clay suspension was added 25 ml of the above pillaring solution dropwise, and pH was adjusted at 8.4 by adding 0.1N NaOH. The slurry was aged at 50°C for 2 days. The pillared clay was separated by centrifugation and washing with deionized water until free of chloride ions.

Triiron intercalation: Zirconia-pillared clay obtained above was added to 37 ml water and stirred overnight. A solution of triiron heptaacetato nitrate complex was added dropwise to the slurry, and stirred for 1 hour. The intercalated clay was separated by centrifugation and washing with deionized water. The residue was dried in vacuo at 105°C. The dried clay was calcined in air at 350°C for 6 hours and ground to -200 mesh (ZPC-Fe_3).

Iron impregnation: Half of the zirconia-pillared clay obtained from above was added to 37 ml deionized water and stirred overnight. A solution of 0lg iron(III) nitrate nonahydrate in 4 ml water was added to the clay slurry and stirred for 5 minutes. To this slurry was added 25 ml of 3% NH_4OH and stirred for 5 minutes. The resulting clay was collected by centrifugation and washing with deionized water. The residue was dried in vacuo at 110°C, calcined at 350°C for 6 hours, and ground to -200 mesh (ZPC-FeOOH).

Preparation of triiron-intercalated and iron-impregnated alumina pillared clay catalyst.

Triiron-intercalated alumina-pillared clay was prepared according to the procedure described previously for DS-.21A.67IPC (4). Triiron-intercalation and iron-impregnation (APC-FeOOH) of the alumina-pillared clay was similar to the zirconia-pillared clay described above. Triiron-intercalation was carried out prior to as well as after calcination of the alumina-pillared montmorillonite (APC-Fe_3).

3.2.1.3 Preparation of Supported Clay Catalysts

Acid treated montmorillonite K-10 (surface area 220-270 m^2/g) obtained from Aldrich Chemical company was used without further purification. Iron hydroxy oxide was supported on acid treated montmorillonite K-10 according to the method of Cugini and co-workers (6). The detailed procedure has been described in our previous report (5). Triiron was also supported on acid washed montmorillonite K-10 using previously described procedure (5). For the preparation of mixed metals supported on K-10, a solution of stannous chloride dihydrate and triiron heptaacetato nitrate was used.

Preparation of ferric sulfate treated K-10

Acid treated montmorillonite, 50 g, was added to 3750 ml deionized water and stirred overnight. A solution of 15.5 g hydrated ferric sulfate (76% $Fe_2(SO_4)_3$) in 400 ml deionized water was added to the clay suspension and stirred for 5 minutes. A solution of 200 g (30% NH_4OH) in 2000 ml water was added to the slurry and stirred for 5 minutes. The final clay was separated by centrifugation and washing with deionized water and dried at 110°C and calcined at 500°C for 3 hours (K-10$Fe_2(SO_4)_3/NH_4OH$).

For the preparation of K-10$Fe_2(SO_4)_3$/Urea, above described procedure was used except that 31 g urea dissolved in 500 ml deionized water was used instead of ammonium hydroxide. The slurry was aged at 90°C for 2 hours. The resulting clay was separated by centrifugation, washed with deionized water, and dried at 110°C in vacuo. A portion of the clay was calcined at 500°C for 3 hours.

3.2.1.4 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.

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

One of the main advantages of pillared clay supports is the potentially large surface areas available between the clay layers for anchoring the active metal sites. To achieve these large areas on the clay support, the pillar density must be small so that the interstitial space is not crowded with pillars. Several methods for limiting the pillar density have been attempted. These include using lower concentrations of the pillaring cations (7), introduction of competing cations (7), and building on an organic pillar framework (8). In the work with the mixed aluminum/iron pillared clays, some low concentrations of aluminum and iron oxycations were used, but the effects on the conversions were insignificant in the different compositions. An alternative that was previously used by Landis and others (8) for preparation of layered titanates with a low density of alumina pillars was adapted for use with the montmorillonites. In this preparation, an organic pillaring reagent (dodecylammonium ions) is introduced to preswell the layered structure, and the inorganic pillaring precursor reagent was then absorbed into the interlayer space. The precursor is tetraethyl orthosilicate (TEOS) or another one of the typical alkyl metalates commonly used in the preparation of ceramics, zeolites, or synthetic clays. The organic pillaring reagent is decomposed and driven out by calcining. Iron was intercalated or impregnated into the pillared clay at various stages of the preparation.

The synthesis of catalysts prepared from both silica and alumina-pillaring of the dodecylammonium montmorillonite was discussed in the previous quarterly technical progress report (4). Some of these large pore montmorillonite catalysts that were prepared earlier were tested in this quarter for hydrocracking activity.

Another alternative for low-density pillars was used to prepare a new catalyst. This technique used polyvinyl alcohol (PVA) as an additive during pillaring with alumina and iron (9). By complexing the intercalated cations in the interstitial space, a greater pore volume can be obtained in the catalyst after calcination to remove the PVA. The pillared clay support had a very low density and was very dark due to a residual of carbon from carbonization of the PVA during calcination. The triiron complex was added to this support and the coated material was calcined.

A low concentration zirconia-pillared montmorillonite was also prepared by intercalation of hydrolyzed zirconyl chloride (7). Calcination gave a low density pillared clay support to which triiron was added, followed by final calcination. Triiron complex was also added prior to calcination of the zirconia pillared montmorillonite. The resulting catalysts were tested for hydrocracking activity.

3.3.2 Testing of Catalysts

3.3.2.1 Catalytic Hydrocracking of Bibenzyl

3.3.2.1.1 Supported Clay 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 (6), 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 (5). 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 pre-sulfidation with H_2 and H_2S (5).

Previous reactions were carried out using 50 wt% of the catalyst at 350°C for 3 hours in the presence of 1000 psig of initial hydrogen pressure. In order to determine optimum reaction time and catalyst loading for high hydrocracking activity, the catalyst prepared by addition of iron nitrate (followed by ammonium hydroxide treatment) to a commercial acid-treated clay (K-10) was tested with bibenzyl as the test compound. The catalysts were sulfided in-situ with CS_2 or elemental sulfur to convert the iron oxide or hydroxyoxide to pyrrhotite. This clay-supported iron catalyst is not expected to be pillared, but contains very small particles of active pyrrhotite when sulfided. The hydrocracking reactions were carried out by heating the substrate with the desired amount of the catalyst at 350°C for the specified time period in the presence of small amount of CS_2 or sulfur and 1000 psi of initial hydrogen pressure. Reaction conditions, conversion data, and major products are given in Table 1.

The three hour reaction of bibenzyl with 50 wt% of iron hydroxyoxide supported on K-10 gave 94% conversion. However, when the same reaction was carried out for one hour heating time, only 39% of bibenzyl was converted into products. The reaction of bibenzyl with 10 wt% of the catalyst for 3 hours reaction time also gave lower conversion (57%) than 50 wt% catalyst described above. 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 the largest products, and the amount of benzene was considerably more than ethylbenzene. 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 (5).

Table 1

CATALYTIC ACTIVITY OF K-10 CLAY-SUPPORTED CATALYSTS

Reaction Temp. = 350°C, CS_2 or Sulfur = 0.03 g, H_2 = 1000 psig

Catalyst (wt. %)	Bibenzyl (mmol)	Reac. Time (hrs)	Conversion (%)	Major Products (mmol)
K-10FeOOH (10)	2.80	3	57	Benzene (1.09) Toluene (0.12) Ethylbenzene (0.44) Indan (0.01) Tetralin (0.01)
K-10FeOOH (50)	2.75	3	94	Benzene (1.75) Toluene (0.46) Methylcyclohexane (0.07) Ethylbenzene (0.85) Ethylcyclohexane (0.02) Indan (0.04) Tetralin (0.07)
K-10FeOOH (50)	2.86	1	39	Benzene (0.90) Toluene (0.17) Ethylbenzene (0.23) Indan (0.02) Tetralin (0.04)
K-10FeOOH[a] (10)	2.75	3	4	Benzene (0.10) Toluene (0.10) Ethylbenzene (trace)
K-10FeOOH[a] (50)	2.81	3	6	Benzene (0.14) Toluene (0.20) Ethylbenzene (trace)
K-10FeOOH[b] (50)	2.76	3	1	Benzene (trace)
K-10FeOOH[c] (10)	2.71	3	18	Benzene (0.23) Toluene (0.10) Ethylbenzene (0.07)
K-10FeOOH[c] (50)	2.85	3	65	Benzene (1.16) Toluene (0.17) Methylcyclohexane (0.02) Ethylbenzene (0.32) Indan (0.03) Tetralin (0.06)

a = Uncalcined K-10FeOOH.
b = Isolated and dried at 110°C after several days of its preparation.
c = catalyst b after calcination.

Compared with same catalyst sulfided in a separate step using a mixture of H_2 and H_2S, the conversion and product yields for the in situ sulfidation were similar. These data are in agreement with those obtained in earlier studies with the mixed pillared clay catalysts. Since the magnitude of the difference in conversion is small, these data demonstrate that in situ sulfidation is a viable alternative to pre-sulfidation in a separate step.

Several different methods were used in the iron impregnation of the clay support. The effects of these techniques used for the preparation of catalysts on the hydrocracking activity were also investigated. The more active catalysts whose activities were described above were prepared by isolation and calcination **immediately** after impregnation.

Another batch of the catalyst was prepared, and the catalyst was dried at 110°C, but not calcined. The reaction of bibenzyl with 10 wt% of the uncalcined catalyst gave very poor conversion (4%). A similar reaction with 50 wt% of this uncalcined also gave only 6% conversion of bibenzyl into products. These results demonstrate the importance of the calcination step in the processing of the iron-clay catalysts. Heating the catalyst at 350°C may be needed to generate strong Bronsted acid sites responsible for aryl-methylene bond cleavages.

In a separate test, an iron-impregnated clay was allowed to remain in the aqueous medium for several days prior to its preparation. This catalyst was then tested for hydrocracking of bibenzyl. The uncalcined catalyst did not display any activity, as indicated by 1% conversion of bibenzyl with 50 wt% of the catalyst. To determine if calcination can improve the activity, the catalyst was calcined at 350°C several days after its preparation. The reaction of bibenzyl with 10 and 50 wt% of calcined catalyst gave 18 and 65% conversions respectively. These results again indicate that calcination of the catalysts is needed for high catalytic activity. Compared with catalyst isolated and calcined immediately after preparation, the catalyst calcined several days after isolation showed significantly poor hydrocracking activity. Hydrolysis/oxidation reactions of the iron that occur during exposure to the water result in lower activities of the subsequently calcined and sulfided catalyst. However, once calcined the catalyst can be stored for longer times without the loss of activity as indicated by the reaction of bibenzyl with catalyst prepared several months earlier.

Ferric sulfate is another iron precursor which is used for coal liquefaction catalysts. Ferric sulfate is converted to a colloidal form by hydrolysis with urea. This procedure leaves a some iron is 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 used for hydrocracking of bibenzyl. Reactions of bibenzyl with 10 wt% of this catalyst were carried out at 350°C for 0.5, 1, and 3 hours in the presence of 1000 psig of initial hydrogen pressure. These reactions gave 6, 14 and 28% conversion of bibenzyl for 0.5, 1 and 3 hours runs respectively (Table 2). Benzene, toluene and ethylbenzene were major products. 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. No explanation for the poor activity of these catalysts is given.

Tin has also been found to be effective for coal liquefaction. 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 with 10 wt% of mixed metal supported catalyst on K-10 at 350°C for 3 hours gave 39% conversion of bibenzyl into mainly benzene, toluene and ethylbenzene. Compared with triiron supported on K-10, the mixed metal supported clay is a poor cracking catalyst.

Table 2

CATALYTIC ACTIVITY OF CLAY-SUPPORTED CATALYSTS

Reaction Temp. = 350°C, CS_2 or Sulfur, H_2 = 1000 psig				
Catalyst (wt.%)	Bibenzyl (mmol)	Time (hrs)	Conversion (%)	Major Products (mmol)
K-10$Fe_2(SO_4)_3$/Urea (10)	2.68	0.5	6	Benzene (0.04) Toluene (0.0.02) Ethylbenzene (trace)
K-10$Fe_2(SO_4)_3$/Urea (10)	2.72	1	14	Benzene (0.20) Toluene (0.18) Ethylbenzene (0.08)
K-10$Fe_2(SO_4)_3$/Urea (10)	2.75	3	28	Benzene (0.93) Toluene (0.14) Ethylbenzene (0.23)
K-10$Fe_2(SO_4)_3$/NH_4OH (10)	2.74	3	5	Benzene (0.11) Toluene 90.01) Ethylbenzene (trace)
K-10Fe_3Sn^{2+} (10)	2.75	3	39	Benzene (0.72) Toluene (0.03) Ethylbenzene (0.10) Indan (0.01) Tetralin (0.01)

3.3.2.1.2 Pillared-Clay Catalysts

Previous results have shown that iron oxide pillars do not survive sulfidation, and layer structure of the clay collapses upon sulfidation resulting in very low surface area solids (2). On the other hand when stable discrete alumina-iron pillared clays were prepared by sequential intercalation of montmorillonite with polyoxy aluminum (Al_{13}) and polyoxy triiron (Fe_3) cations, the catalytic activity is improved (Table 3 and 4). The increased activity is due to strong acid sites associated with alumina pillars. Previous results have also shown that mixed pillared-montmorillonite gave high conversions of bibenzyl into low molecular weight products. However, large amounts of catalysts (50 wt%) were used in the previous hydrotreating reactions (4). The minimum catalyst concentration, reaction time, reaction temperature and hydrogen pressure needed for reasonably good conversions of coals as well as model compounds need to be determined. During this period, studies have been conducted to determine minimum catalyst loading and reaction time required to achieve good conversion of bibenzyl into products. The reactions of bibenzyl with various catalyst loading (10-50 wt%) and reaction time (1-3 hours) have been carried out at 350°C 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 Tables 3 and 4. The catalysts were recovered in almost quantitative amounts, and no retrograde reactions or coke were observed during reactions.

Reactions of bibenzyl with in situ sulfided triiron-intercalated alumina-pillared clay (APC-Fe_3) gave 84, 83, and 87% conversion of bibenzyl into products for 10, 20 and 50wt% catalyst loadings respectively (Table 3). Product distribution was similar for all three reactions. Major products were benzene, toluene and ethylbenzene. The ratio of benzene to ethylbenzene was ca. 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 on 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. Unlike alumina-pillared clay, conversion to high boiling condensation products was minimal. It was expected that the main activity of the iron sulfide sites would be to activate hydrogen, whereas the pillared clay would contain the acidic sites responsible for the cracking mechanism. These reactions show that 10 wt% of catalyst is sufficient to achieve high hydrocracking activity of pillared clay catalyst. They also demonstrate that the pillared clay supported catalysts are significantly better than those prepared with simple acid-washed clay (K-10) at low catalyst concentrations.

The reaction of bibenzyl with 10 wt% of triiron-intercalated alumina-pillared clay for 1, 2, and 3 hours gave 68, 71, and 84% conversion respectively of bibenzyl into products. Major products were benzene, toluene and ethylbenzene. The ratio of benzene to ethylbenzene was 3-5. Longer reaction time gave lower ratio of benzene to ethylbenzene. These reactions indicate that longer reaction time (3 hours) is needed to obtain high yield of low molecular weight components from hydrocracking of bibenzyl.

Table 3

EFFECTS OF CATALYST CONCENTRATION ON REACTIONS WITH MIXED PILLARED CLAY CATALYSTS

Reaction Time = 3 hrs, Reaction Temp. = 350°C, H_2 = 1000 psig, CS_2 or S = 0.03 g			
Catalyst (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
APC-Fe_3 (10)	2.86	84	Benzene (1.77) Toluene (0.41) Ethylbenzene (0.57) Indan (0.04) Tetralin (0.07) Naphthalene (0.02) o-Xylene (0.01)
APC-Fe_3 (20)	2.80	83	Benzene (1.95) Toluene (0.17) Ethylbenzene (0.66) Indan (0.05) Tetralin (0.07)
APC-Fe_3 (50)	2.47	87	Benzene (1.99) Toluene (0.21) Methylcyclohexane (0.05) Ethylbenzene (0.80) Ethylcyclohexane (0.02) Indan (0.03) Tetralin (0.05)

APC-Fe_3 is the catalyst prepared by pillaring Na-montmorillonite with polyoxy (Al_{13}) aluminum cations, and then intercalating triironheptaacetato complex prior to calcination.

Table 4

EFFECTS OF REACTION TIME
ON REACTIONS WITH MIXED PILLARED CLAY CATALYSTS

Reaction Temp. = 350°C, H_2 = 1000 psig, CS_2 or S = 0.03 g				
Catalyst (%)	Reac. Time (hrs)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
APC-Fe_3 (10)	1	2.75	68	Benzene (1.53) Toluene (0.11) Ethylbenzene (0.29) Indan (0.03) Tetralin (0.04)
APC-Fe_3 (10%)	2	2.75	71	Benzene (1.60) Toluene (0.16) Methylcyclohexane (0.01) Ethylbenzene (0.36) Indan (0.04) Tetralin (0.05)
APC-Fe_3 (10)	3	2.86	84	Benzene (1.77) Toluene (0.41) Ethylbenzene (0.57) Indan (0.04) Tetralin (0.07) Naphthalene (0.02) o-Xylene (0.01)

The effect of pillaring techniques on the hydrocracking activity was determined by comparing the alumina-iron-pillared clays prepared by two different methods. Na-montmorillonite was pillared with polyoxy aluminum cations. Triiron was then intercalated into alumina-pillared clay before and after calcination. The alumina-iron pillared clays (APC-Fe_3) were in situ-sulfided and reacted with bibenzyl under the above conditions. The catalysts prepared by triiron intercalation into uncalcined alumina-pillared clay gave a somewhat higher conversion (84%) of bibenzyl than the catalyst from triiron intercalation into calcined alumina-pillared clay (79%) (Table 5). Product distribution was similar for these two catalysts.

Table 5

EFFECT OF PREPARATION METHOD ON THE CATALYTIC ACTIVITY OF MIXED PILLARED CLAYS

Reaction Temp. = 350°C, CS_2 or S = 0.3 g, H_2 = 1000 psig

Catalyst (wt.%)	Bibenzyl (mmol)	Reaction Time (hrs)	Conversion (%)	Major Products (mmol)
APC-Fe_3 (10)	2.86	3	84	Benzene (1.77) Toluene (0.41) Ethylbenzene (0.57) Indan (0.04) Tetralin (0.07) Naphthalene (0.02) o-Xylene (0.01)
APC-Fe_3^* (10)	2.75	3	79	Benzene (1.81) Toluene (0.17) Ethylbenzene (0.57) Indan (0.05) Tetralin (0.08)
APC-FeOOH (10)	2.75	3	34	Benzene (0.54) Toluene (0.05) Ethylbenzene (0.04) Indan (0.02) Tetralin (0.01)
ZPC-Fe_3 (10)	2.75	3	66	Benzene (1.37) Toluene (0.12) Methylcyclohexane (0.01) Ethylbenzene (0.28) Indan (0.04) Tetralin (0.06)
ZPC-FeOOH (10)	2.80	3	40	Benzene (0.88) Toluene (0.21) Ethylbenzene (0.24)

* = Alumina-pillared clay was calcined prior to addition of triiron complex.

The effect of the types of pillars used for the preparation of alumina-iron-pillared clays was also investigated. Triiron-intercalated zirconia-pillared clay was prepared and tested for the hydrocracking activity using bibenzyl as the test compound. The reaction of bibenzyl with 10 wt% catalyst gave 66% conversion of bibenzyl into smaller products. Major products were benzene, toluene and ethylbenzene. The ratio of benzene to ethylbenzene was 4. Compared with triiron-intercalated alumina-pillared clay, triiron-intercalated zirconia-pillared clay is a poor hydrocracking catalyst. The lower activity of triiron-intercalated zirconia-pillared clay may be due to the lower Bronsted acidity of zirconia pillars compared with alumina pillars.

In a previous section, the activity (at 10% catalyst concentration) of the catalyst prepared by triiron intercalation into alumina-pillared clay (mixed iron/alumina-pillared clay) was demonstrated to be substantially higher than the activity of the catalyst prepared by triiron impregnation into acid-washed K-10 clay. It was also of interest to compare the activity of the mixed iron/alumina-pillared catalysts with catalysts prepared by impregnation of iron as ferric nitrate into the alumina- and zirconia-pillared clays, followed by treatment with ammonium hydroxide (iron hydroxyoxide form). Reactions of bibenzyl with iron hydroxy oxide impregnated alumina- and zirconia-pillared clays gave 34 and 40% conversions respectively. The poor hydrocracking activities of catalysts prepared by this treatment might be attributed to the same deleterious hydrolysis effect noted earlier for other poor catalysts.

In order to determine the effect of surface area and pore size on the catalytic activity of pillared clays, organic pillaring reagent (dodecylammonium ions) was introduced to preswell the layers prior to pillaring with oxymetal ions via the alkoxymetals (TEOS or aluminum isopropoxide). The organic pillaring agent was then decomposed by calcination. The pillared clays were then intercalated with triiron complex or impregnated with iron nitrate. The catalytic activity was investigated by reacting with bibenzyl. Reaction conditions and analytical data are given in table 6.

The reaction of bibenzyl with 10 wt% of iron nitrate-impregnated alumina-pillared DAM gave 24% conversion of bibenzyl into products, mainly benzene, toluene and ethylbenzene. However, when the same reaction was carried out with 10 wt% of iron-nitrate-impregnated silica-pillared DAM, the conversion was considerably higher (60%). Similar reaction using 50 wt% of the catalyst gave significantly higher conversion (75%). Product yield was also considerably higher. Iron hydroxy oxide supported on silica-pillared DAM gave very poor conversion of bibenzyl (2%). Triiron-intercalated silica-pillared DAM was also prepared in DMF and tested for the hydrocracking of bibenzyl using 10 wt% catalyst. This reaction gave only 25% conversion of bibenzyl.

Catalysts were also made using a support prepared by calcining a polyvinyl alcohol-complexed alumina-pillared clay. Triiron was then intercalated into the calcined clay and recalcined. The resulting large pore catalyst was tested before and after the second calcination. Reaction of bibenzyl were carried out with 10 wt% of uncalcined and calcined catalysts. Calcined as well as uncalcined catalysts gave very poor conversions of bibenzyl (Table 6). Calcination slightly improved the activity of the catalyst.

Table 6

CATALYTIC ACTIVITY OF LARGE PORE PILLARED CLAYS

Reaction Temp. = 350°C, Reaction Time = 3 hrs, CS_2 or S = 0.03 g, H_2 = 1000 psig

Catalyst (wt.%)	Bibenzyl (mmol)	Conversion (%)	Major Products (mmol)
PVA-APC-Fe_3 (10)	2.75	5	Benzene (0.15) Toluene (0.01) Ethylbenzene (0.01)
PVA-APC-Fe_3[a] (10)	2.80	14	Benzene (0.2) Toluene (0.2) Ethylbenzene (0.02)
DAM-AP-Fe^{3+} (10)	2.67	24	Benzene (0.27) Toluene (0.05) Ethylbenzene (0.05)
DAM-SP-Fe^{3+} (10)	2.62	60	Benzene (0.44) Toluene (0.07) Ethylbenzene (0.08) Indan (0.01) Tetralin (0.02)
DAM-SP-Fe^{3+} (50)	2.79	75	Benzene (1.27) Toluene (0.36) Methylcyclohexane 90.03) Ethylbenzene (0.43) Ethylcyclohexane (0.0.01) Indan (0.03) Tetralin (0.05)
DAM-SP-Fe_3-DMF (10)	2.69	25	Benzene (0.26) Toluene (0.03) Ethylbenzene (0.02)
DAM-SP-FeOOH (10)	2.83	2	Benzene (trace) Toluene (0.02)

a = calcined after Fe_3 intercalation

3.3.2.2 Catalytic Hydrotreating of Pyrene

Catalytic hydrotreating of pyrene was investigated to determine the activity of the sulfided pillared clay catalysts for hydrogenation and hydrocracking of polynuclear aromatic systems common to most coals. Previous results have shown that in situ sulfided mixed (Fe and Al) pillared-clay using 50 wt% loading is an effective hydrogenation catalyst for pyrene. However, the hydrocracking activity was low (36%) 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 (5). Hydrotreating was carried out with 10 wt% of freshly made pillared clay 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 7.

Table 7

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)
APC-Fe_3 (10)	76	Hexadecahydropyrene (3 isomers)(0.02) 1,2,3,3_a,4,5,9,10_a,10_b-Decahydropyrene (0.07) 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 (0.28) 1,2,3,6,7,8-Hexahydropyrene(0.42) 4,5,9,10-Tetrahydropyrene (0.13) 4,5-Dihydropyrene (0.50) Cracked Products (17%)

The reaction of pyrene with the mixed pillared montmorillonite (APC-Fe_3) gave a high conversion (76%) of pyrene into products. The majority of the products were di-, and hexahydropyrenes. Since we did not calibrate for these isomers, data are derived from FID assuming the response factors of pyrene and hydropyrenes to be the same. Relatively small amounts of hexdecahydro-, decahydro- and tetrahydropyrenes were also formed. Hydrogenation activity was similar to that of iron hydroxyoxide supported on acid washed montmorillonite pre-sulfided with H_2S and H_2 (5), indicating the effectiveness of in-situ sulfidation with CS_2. It is important to note that with the in situ-sulfided catalyst, substantial amounts of lower molecular weight components (about 17% 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.

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