FINE PARTICLE CLAY CATALYSTS FOR COAL LIQUEFACTION

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by

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1.0 EXECUTIVE SUMMARY

Methods for the production and testing of iron-pillared clay catalysts were investigated in this quarter. Intercalation of polyoxy triiron cations into sodium montmorillonite gave precursor iron-exchanged clays that were separated into fine particles and large particles by using high speed centrifugation. The precursor clays were calcined to generate the iron-pillared montmorillonites. X-ray diffraction showed that different iron oxide compositions were present in the two calcined iron-pillared materials. The iron-pillared clays were sulfided and used in preliminary hydrocracking tests with bibenzyl. Sulfided iron-pillared montmorillonite catalysts effectively catalyzed the cleavage of aryl-alkyl bonds in bibenzyl under mild hydrogenation conditions, the larger particles being more active. High conversions of bibenzyl to benzene, ethylbenzene, and a large number of minor products were obtained. Part of the single-ring aromatics produced from the catalytic hydrocracking of bibenzyl were hydrogenated to give cycloalkanes. Based on the products of the hydrotreating reactions, a Brønsted acid-catalyzed aryl-carbon bond cleavage is suggested. Some Lewis-acid catalysis was also indicated.

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 initiated. 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 the two dimensional chemistry in the interlayer space 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 combine the roles of the pillaring agent and catalytic site by using iron sulfides to pillar the clay.

Work in the first quarter was concerned with preparation methods for the iron-pillared montmorillonites. The montmorillonite used in this work was previously used successfully in chromia-pillaring experiments at UNDEERC. The sodium form of this clay 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. The metal-exchanged clay is subsequently calcined to form the stable pillars. At this point the metal will be highly dispersed as intercalated polyoxymetal cations. It is likely that calcining will affect the dispersibility of the clay particles. The relationship between preparation methods, starting materials (clay type and iron type), initial particle sizes, and resulting catalytic activities will be determined in subsequent studies.

3.2 Experimental

3.2.1 Iron-Pillared Montmorillonite Catalyst Preparation

3.2.1.1 Purification of Smectite Clay

Sodium montmorillonite from Clay Spur, Wyoming, USA, contains carbonates, free ferric oxide and organic matter which must be removed in order to simplify and standardize the evaluation of clay catalysts. Soluble salts and carbonates are removed from the clay in order to promote flocculation of the clay. Calcium carbonate and free (non-lattice) iron oxides may act as a cementing agent preventing intercalation of the desired metal oxide species.

The clay (Na-montmorillonite) was ground to 200-325 mesh size and 50 g were suspended in 500 ml of 1N sodium acetate buffered with acetic acid ($\text{pH}=5$), and digested for one hour at 70°C with occasional stirring. The clay was separated by centrifugation and redigested with fresh buffer solution. The treated clay was added to 400 ml of 0.3N sodium citrate and 50 ml of 1N sodium bicarbonate, and heated to 75-80°C. At this point 10 g of sodium thiosulfate was added slowly and the temperature was carefully kept within this range for 30 minutes so that free iron oxides could be removed. The solution was cooled to room temperature, centrifuged and washed with water. The resulting clay was digested with 10 % sodium peroxide for 2 hours to remove the organic matter. At this point the clay was sodium saturated by addition of sodium chloride, and centrifuged. The clay was washed with deionized water until free of chloride ions and air dried.

3.2.1.2 Preparation of pillaring reagent

Trinuclear acetato-hydroxo iron(III) nitrate, $[\text{Fe}_3(\text{OCOCH}_3)_7\text{OH}\cdot 2\text{H}_2\text{O}]\text{NO}_3$, was prepared according to the method reported by Yamanaka et al. (2).

A solution of 80.8 g of iron(III) nitrate $[\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}]$ dissolved in 50 ml of absolute ethanol was placed in a 500 ml two-necked round-bottomed flask, equipped with a reflux condenser and a dropping funnel. To this solution, 140 ml of acetic anhydride was added dropwise with vigorous stirring. When the reaction started with the evolution of heat, the flask was cooled in ice. After the addition, the mixture was stirred for two hours at ice bath temperature. The resulting precipitate was separated by filtration and dried by heating in vacuo at 50°C overnight.

3.2.1.3 Pillaring Reaction

A 0.04 M aqueous solution of the trinuclear acetato complex (17.4 g) was added dropwise with vigorous stirring to a 1% suspension of Na-montmorillonite in deionized water. After the addition of acetato complex, the mixture was allowed to react with occasional stirring at 35°C for 3 hours. After the suspension was left for three hours, the montmorillonite was centrifuged at 3000 rpm and washed with water several times, and dried by evacuation at 40°C (78 % yield based on starting clay). The resulting product was brown in color and will be referred to as large particle iron-pillared clay, (LPIPC). The

supernatant and washings were further centrifuged at high speed (15000 rpm) and washed with water several times, and dried by evacuation at 40°C (22 % yield). The resulting product was brown as before and will be referred as fine particle iron-pillared clay (FPIPC). The iron-pillared clay products were calcined in air at 350°C for 6 hours.

Detailed characterization of the iron-pillared clays by acidity studies, IR, TGA, elemental analyses, particle size, surface area/pore size, Mössbauer spectroscopy, and XRD is in progress and will be reported in our next quarterly report.

3.2.1.4 Sulfidation of Catalysts

The calcined catalyst precursor was placed in a 10 ml. microreactor. The microreactor was evacuated, pressurized with 200 psi of H₂S, and placed in a rocking heater preheated to 350°C. The heating was continued for 3 hours. The reactor was then cooled to room temperature, degassed, and the sulfided catalyst was stored in air-tight ampoules.

3.2.2 Analytical procedures and Instrumentation

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol capillary column. A mixture of 2,2,4-trimethylpentane and n-octadecane was the internal standard. GC/FTIR/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron film of DB-5.

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

3.2.3 Catalytic hydrotreating

In a typical run, 0.50 g of the test compound and 0.25 g of the desired catalyst were placed in a microreactor (tubing bomb). The microreactor 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 dichloromethane, 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 Iron-Pillared Clays

The sodium form of montmorillonite exists in a very finely dispersed state in a low ionic strength neutral aqueous medium. The aluminosilicate layers of the clay are believed to be separated to the extent that ion exchange of associated cations is relatively unhindered. Iron was introduced as the triiron acetato complex monoanion (2). Earlier work with ferric salts gave clays in which the iron was not intercalated but was associated with outer layers (3). Intercalation of the iron resulted in a 78% yield of larger iron-intercalated particulates that were collected by centrifugation and washed with water. The supernatant and washings were then centrifuged at high speed to collect the fine particles (22% yield). The two iron-intercalated fractions were calcined to give the iron-pillared clay catalyst precursors (LPIPC and FPIPC) used in current tests.

3.3.2 Characterization of Iron-Pillared Clays

Iron-pillared montmorillonite catalyst precursors were characterized by X-ray diffraction (XRD) analysis. Since pillared clays usually show only broad XRD patterns, the use of oriented specimens is helpful for measuring the basal spacing unambiguously. In addition to preferred orientation, XRD analysis using random orientation was also performed.

Fig. 1 shows the XRD 2θ plots of the large as well as fine particle iron-pillared montmorillonites obtained after calcining. A significant difference in the composition of the iron sites is evident. Both samples exhibit lines corresponding to hematite and maghemite (both Fe_2O_3); however, the fine particle clay contains hematite in much greater abundance, whereas the large particle material contains very little hematite. The formation of these different compositions during the calcination of the metal-exchanged clays may be attributed to partial hydrolysis of the triiron clusters during washing and collection procedures. The fine particles were exposed to water for a greater period of time. These data appear to be similar to those obtained by Lee for pillaring with hydrolyzed ferric chloride, which indicated that hematite particles had formed (4). The d_{001} peak corresponding to the interlayer spacing was quite broad in the 2θ plot for both samples. This may indicate that the spacings are irregular (5) in the calcined products.

Further analyses such as particle size, surface area, acid sites, infrared, Mossbauer, and thermogravimetric are in progress.

3.3.3 Testing of Iron-Pillared montmorillonite Catalysts

The iron-pillared clay precursors prepared by calcination of the two different particle size intercalated clays were converted to the sulfide form by standard procedures. Catalyst activity of the sulfided iron-pillared clay catalysts were tested by reacting with bibenzyl as the probe molecule. Reactions were carried out at 350°C for 3 hours in the presence of 1000 psi of molecular hydrogen in a rocking autoclave reactor. Conversion data and major products are presented in Table 1.

Figure 1: X-Ray Diffraction 2 θ Plots: 1. LPIPC; 2. FPIPC

TABLE 1
CATALYTIC HYDROTREATING OF BIBENZYL

Reaction Time = 3 hrs, Reaction Temp. = 350°C, H ₂ = 1000 psi, Catalyst wt./Substrate wt. = 0.5			
Catalyst (g)	Substrate (mmol)	Conversion (%)	Major Products (mmol)
LPIPC	2.73	80.3	Benzene (1.79) Toluene (0.14) Ethylbenzene (0.51)
FPIPC	2.73	62.3	Benzene (1.20) Toluene (0.09) Ethylbenzene (0.28)

The conversions of bibenzyl with two sulfided iron-pillared clay catalysts were 80.3 and 62.3 for LPIPC and FPIPC respectively. Examination of the products obtained from the reactions of bibenzyl with the two catalysts indicated significant hydrocracking activity for both of these catalysts. The products included many hundreds of components, indicative of rearrangements and hydrogen addition as well as hydrocracking. These results indicate that iron-pillared clay catalysts are effective in cleaving aryl-methylene and other C-C bonds at lower temperature.

The major products were benzene, toluene, and ethyl benzene. Benzene and ethylbenzene were the largest products; the ratio of benzene to ethylbenzene was 3.5. These products are indicative of the Brönsted acid catalysis mechanism, which involves ipso protonation of an aromatic ring of bibenzyl, followed by aryl-methylene bond cleavage to form benzene and phenylethyl carbonium ion. The phenylethyl carbonium ion is reduced to ethylbenzene by hydride transfer or hydrogenation or could undergo a variety of reactions to give other products. Ethylbenzene is further cleaved to benzene and ethane by the same process; thus, the ratio of benzene to ethylbenzene is much greater than 1.0. This reaction mechanism is common in reactions catalyzed by clays and clay-supported catalysts. The formation of toluene probably occurs via a Lewis acid catalyzed mechanism, since the temperature is too low for homolytic cleavage of the central bond in bibenzyl. Reduction of carbonium ion intermediates in the reaction may or may not involve the iron sites. Iron sulfides can participate in hydrogen transfer reactions, but the mechanism is still unknown.

In addition to the hydrocracked products described above, several hydrogenated products were also formed in the iron-pillared clay-catalyzed reactions of bibenzyl. Minor components observed in the reaction products were propylbenzene, butylbenzene, tetralin, ethylbibenzyl, and

phenylethylbibenzyl, etc. The alkylbenzene products resulted from hydrogenation of the bibenzyl, followed by cracking reactions, probably involving Lewis acid sites. It is likely that the iron sulfide (pyrrhotite) sites activated hydrogen for transfer to the aromatics or complexed aromatics. Very small amounts of cyclohexane, ethylcyclohexane, and phenylethylcyclohexane were formed from hydrogenation of the aromatic rings. However, a substantial amount of methylcyclohexane was formed, probably from cleavage of the tertiary carbonium ion derived from phenylethylcyclohexane (or hydrogenation of ring-protonated bibenzyl). The two catalysts were almost identical in the proportion of ring-hydrogenated components found in the reaction products.

Some of the reaction products were addition products of bibenzyl that may be regarded as Friedel Crafts addition products. However, extensive condensation reactions and coke formation were not observed in the reaction. In comparison, the acidic clay catalysts gave larger amounts of condensation products. The behavior of the sulfided iron-pillared clay appears to be more consistent with that of molybdenum sulfide loaded clays that give much less condensation reaction. Thus, the iron sulfide (pyrrhotite) sites in the clay may have a beneficial effect in activating hydrogen for transfer to the carbonium ions, so that this reaction can compete favorably with the condensation or addition reactions. Whether this reaction occurs via hydride, hydrogen atom, or some other mechanism is unknown. GC/FTIR/MS analyses are in progress to determine the exact composition of the hydrotreated products.

The lower cracking activity of the smaller pillared clay particles (FPIPC) in the conversion of bibenzyl may have resulted from hydrolysis of the triiron clusters bound to the clay layers during the washing and centrifuging operations. According to the X-ray diffraction results, the composition of the large and the fine iron particles obtained after calcining differed significantly (see discussion above). The maghemite in the large particles may have given a different composition of iron sulfide than did the hematite in the fine particles. A hydrolysis of the iron may also have somehow affected the subsequent pillaring or possibly the acidic sites in the clay structure that developed when the clays were calcined. In the discussion above, the similarity in the proportion of hydrogenation products formed using the two catalysts was pointed out; only the cracking abilities differed for the catalysts. It is certain that more than surface area is involved in determining the activity of the iron-pillared clay catalyst particles.

Future work involves alternative methods for forming and collecting the fines, especially more rapid collection. Other studies include examining the effect of pH, ionic strength, stirring or shear rate, acetate (or other salt) concentration, alternative solvents, and other treatments of the metal-exchanged clay prior to calcining. Hydrogenation of multiring systems is, of course, more important to coal liquefaction than hydrogenation of single ring compounds; hence, a test for this activity will be carried out with all the new catalyst preparations.

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