

CATALYTIC REACTIONS OF SULFIDED IRON- AND MIXED METAL-PILLARED CLAYS

Edwin S. Olson and Mary L. Yagelowich
Universal Fuel Development Associates, Inc.
Grand Forks, ND 58201

and

Ramesh K. Sharma
University of North Dakota Energy and Environmental Research Center
Grand Forks, ND 58202

Key words: catalysts, pillared clays, coal liquefaction

ABSTRACT

Iron-pillared montmorillonites were prepared by several methods and tested in hydrocracking and hydrogenation reactions. Rapid collection of the iron-intercalated clays was necessary for maximum activities, as was removal of residual sodium ions by exchange with ammonium ions. Calcination and sulfidation of the iron-pillared clays resulted in the formation of pyrrhotite, much of it in particles large enough to exhibit sharp XRD peaks. Thus the iron tends to migrate from its originally dispersed state, and surface area decreases with collapse of the layers. Alumina-pillaring prior to, or simultaneously with, intercalation of the iron resulted in more stable catalysts. The combined effects of clay acidity and hydrogen activation by the pyrrhotite resulted in high conversions in hydrocracking and hydrogenation tests. The presence of pyrrhotite resulted in minimal coking and condensation reactions.

INTRODUCTION

The goal of the UFDA catalyst research program is the development of disposable, highly dispersed, high surface area catalysts for the direct liquefaction of coal. 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 ($<2 \mu$), appreciable surface area for adsorption of organic molecules, and unique intercalating capabilities. Hence, they are utilized 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 1960s they were replaced by more thermally stable and selective zeolite catalysts.

The use of large stable cations to pillar the aluminosilicate layers of clays 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 that of most of the zeolites. Therefore, these pillared clay catalysts may be more effective in cracking the large coal macromolecules than the conventional catalysts. The intent of this work is to discover how to obtain finely dispersed iron sulfide (pyrrhotite) catalytic sites in the pillared clay structure that will be useful for coal liquefaction.

RESULTS AND DISCUSSION

Initial work was concerned with preparation methods for iron-pillared montmorillonites. The sodium form of this clay disperses to an extremely fine particle size in an aqueous medium with low concentrations of base. This form was preferred for metal ion exchange reactions that give the intercalated clays, since the clay layers are highly separated in this state and mass transfer is rapid. Iron in the form of a polyoxytriiron (III) complex (heptaacetatohydroxytriiron nitrate) was exchanged for the interlayer cations of the dispersed sodium montmorillonite (2). The iron-exchanged clays were subsequently calcined to form the stable polyoxyiron cation-pillared clays. For creation of catalytic sites for activation of hydrogen, the oxyiron species were converted to sulfide forms by treatment with hydrogen sulfide or carbon disulfide.

Intercalation of polyoxytriiron resulted in a change in particle-size distribution, with a substantial portion of larger particles (78%) being formed by agglomeration of the very fine particles. A fine particle fraction was also isolated by high-speed centrifugation. Calcination of the two fractions gave materials consisting of larger particles. X-ray diffraction studies of both calcined catalyst precursor fractions showed that hematite and maghemite (both Fe_2O_3) had formed. The material from the fine clay particles contained hematite in greater abundance than that from the larger particles. The formation of these different compositions during the calcination of the iron-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 much greater period of time. These data appear to be similar to those obtained by Lee and others (3) for pillaring with hydrolyzed ferric chloride, which indicated that hematite particles had formed. The d_{001} peak corresponding to the interlayer spacing was quite broad in the 2θ plot for both samples, indicating that spacings are irregular in the calcined products.

The difference in iron oxide composition between the calcined fine and larger particles of intercalated clay was further investigated by using a more rapid method in collection of the fine particles. X-ray diffraction of the calcined clays from the fine particles had a much smaller amount of hematite than the clay prepared by the former method. Thus the 2θ plots of catalyst precursors obtained from both the fine and larger particles in this preparation were very similar.

Methods for conversion of the oxyiron-intercalated clays to active sulfide forms were compared. Sulfidation was carried out either by heating the calcined precursor with a mixture of H_2S (100 psi) and H_2 (900 psi) in the rocking heater at 400°C for 2 hr or by in situ reaction with 40 mg of carbon disulfide that was added with the test compound, decalin solvent, or coal, depending on the reaction being carried out. The catalysts prepared by treatment with H_2S exhibited major peaks corresponding to pyrrhotite. The pyrrhotite peaks were relatively narrow, indicating that the particle size of the iron sulfide in the catalyst may be larger than desired for high catalyst activity. Sulfidation under these conditions may have mobilized the iron in the pillars so that some larger iron sulfide particle formed, as described by Lee and others (3). In contrast, the

catalysts activated by in situ treatment with CS_2 did not show significant peaks for pyrrhotite or pyrite. Since sulfidation did occur, the iron sulfide species in these catalysts must be very minute. As described below, these catalysts had superior hydrocracking activities.

When sulfidation was carried out with larger amounts of H_2S , x-ray diffraction showed that much of the iron was converted to pyrite rather than pyrrhotite. The pyrite-containing catalyst was easily converted back to the pyrrhotite form by further treatment with hydrogen at 400°C .

Surface areas of the fine particle and large particle iron-pillared clay catalysts were 156 and $181 \text{ m}^2/\text{g}$, respectively. However, on sulfiding the fine particle iron-pillared clay catalyst in H_2S and H_2 at 400°C for 2 hours, the surface area dropped to $17 \text{ m}^2/\text{g}$. The reduction in surface indicates an undesired collapse of the interlayer structure or formation of iron sulfide agglomerates.

Hydrocracking activities of iron-pillared clay catalysts were determined by reacting with bibenzyl as the test compound. Reactions were carried out at 350°C for 3 hours in the presence of 1000 psi of molecular hydrogen in a 10-ml rocking autoclave reactor. The catalysts were recovered in quantitative amounts, and no retrograde reactions or coke were observed during reactions.

Comparison of the bibenzyl hydrocracking results for the initial sulfided catalysts prepared from the fine and larger iron-pillared clay particles showed that the catalyst from the hematite-containing fines had a much lower activity (62% conversion) than the catalyst from the large particles (80% conversion). The lower activity of the catalyst from the fines was attributed to hydrolysis reactions that occurred prior to calcining. For the second batch of pillared clays that were rapidly collected, the bibenzyl hydrocracking activities of the sulfided catalysts were essentially identical for the fine and larger particles (79 and 80% conversion, respectively). This observation was consistent with the low hematite content of both precursors as demonstrated by the similar 2θ plots described above.

Examination of the products obtained from the reactions of bibenzyl with sulfided iron-pillared clays provided information on the nature of the hydrocracking activity for the catalysts. 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, indicating the further cracking of the ethylbenzene to benzene. These products are indicative of the Brönsted acid catalysis mechanism. The mechanism involves the 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 it could undergo a variety of reactions to give other products. 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.

The bibenzyl cracking products included many hundreds of other components, indicative of rearrangements and hydrogen addition as well as hydrocracking. Part of the single-ring aromatics was hydrogenated to give cycloalkanes in the reactions with sulfided catalysts. A substantial amount of methylcyclohexane was formed, probably from cleavage of the tertiary carbonium ion derived from

phenylethylcyclohexane or hydrogenation of the ring-protonated bibenzyl. Minor components formed as a result of hydrocracking were propylbenzene, butylbenzene, tetralin, ethylbibenzyl, and phenylethylbibenzyl, etc. The alkylbenzene products resulted from hydrogenation of bibenzyl followed by cracking reactions, probably involving Lewis acid sites.

A second factor in determining the activity of the catalysts was the concentration of iron introduced into the clay. Use of a smaller amount of iron might result in a lower number of pillars and, consequently, result in a larger micropore volume. Exchange of one-third of the total equivalents of sodium by the triiron acetate cation rather than using an excess of the triiron gave a catalyst, after calcination and sulfidation of the large particle fraction, that was as active in hydrocracking reactions (79% conversion) as the catalyst prepared previously with excess triiron complex. The fine particle fraction had a lower activity (33% conversion).

The presence of excess sodium in the catalyst brings up a question regarding the possible loss of Brönsted acid sites due to the presence of sodium cations. The sodium ions were exchanged out of one of the clays (from the fine particles) with ammonium ions following the iron-exchange. Calcination of this precursor to drive off ammonia gave a more active catalyst (64% conversion compared with 33%), because of regeneration of the Brönsted acid sites.

A comparison of the sulfided versus nonsulfided forms of the iron-pillared clays showed that the nonsulfided forms had a much lower hydrocracking activity (36 and 40% conversions for fine and large particles, respectively). These values are consistent with those obtained for other clay supports. Major products from nonsulfided catalysts were the same as those obtained with sulfided catalysts. The major difference in activity for the nonsulfided clays was the lower conversion, lower amounts of cyclohexanes, and lower proportion of ethylbenzene. Some of the reaction products were addition products of bibenzyl that may be regarded as Friedel Crafts addition products. However, extensive condensation and coke formation were not observed in the reaction. In comparison, acidic clay catalysts gave larger amounts of condensation products. Our results indicate that iron-pillared clays are effective in cleaving aryl-methylene and other C-C bonds at lower (350°C) temperature.

A general problem with the iron-pillared clays is that the calcination and/or sulfidation treatments appear to mobilize the iron and generate particles of the iron oxide and sulfide that are larger than desired for maximum utilization of the iron. Surface areas are also substantially decreased, owing to collapse of the layer structure. The use of discrete mixed alumina/iron-pillared clays or of alumina-pillared clays as supports for pyrrhotite active sites may give a more effective particle size for the iron sites and more stable pillared structures. The aluminum pillars are stable to calcining and sulfidation treatments.

Aluminum pillars were introduced by treatment of sodium montmorillonite dispersions with the oxaluminum cation, and various methods were investigated for intercalation of the iron. Several pillared clay catalysts with discrete pillars composed of alumina and of iron oxide were prepared by intercalation of sodium montmorillonite first with oxaluminum cations and then with oxiron cations (sequential pillaring). These materials differed in the amounts of alumina and iron oxide introduced. After calcining and sulfiding with hydrogen sulfide/hydrogen mixture, these catalysts exhibited high activities, with conversions of 85 to 88% in hydrocracking tests with bibenzyl. Neither the

concentration of alumina or iron had a significant effect on the activities, and a relatively low iron concentration (500 ppm) was quite active in the tests.

A second method for preparation of the discrete pillars was utilized. In this method, the oxyaluminum cations and the oxyiron cations were added simultaneously to the sodium montmorillonite in large excess. The catalyst obtained by calcining and sulfiding as above was nearly equally effective in hydrocracking tests with bibenzyl (83% conversion). Thus either the simultaneously or sequentially mixed pillared clays gave stable clays containing effective concentrations of pyrrhotite and acidic sites for catalysis.

The third method for preparing mixed pillared clays utilized a mixed oxymetal cation complex composed mainly of aluminum with a small amount of iron. This alloy-pillaring gave a catalyst with lower activity in hydrocracking tests (72% conversion). X-ray diffraction showed that iron from the alloy pillar had been converted to pyrrhotite by the sulfidation; hence, the lower activity is probably due to some collapse of the pillared structure during this transformation of the iron.

Since the presence of sodium ions was found to exert a significant negative effect on hydrocracking conversion, one of the sequentially pillared catalysts was treated with ammonium nitrate in order to exchange out any remaining sodium ions. After calcination to volatilize the ammonia and sulfidation, the catalyst gave a slightly better conversion in the bibenzyl hydrocracking test (89%).

The method of sulfiding the iron in the mixed metal-pillared catalyst was also varied. By adding a small amount of carbon disulfide to the reaction rather than presulfiding the catalyst with hydrogen sulfide/hydrogen, a significantly higher conversion of bibenzyl was obtained (94%). The reason for higher activity is suspected to be that the pyrrhotite particle size is smaller with this method of sulfiding (see discussion above).

In addition to effective catalysis of hydrocracking reactions at moderate temperatures, the iron-pillared clays were effective catalysts for catalyzing the hydrogenation of pyrene. Hydrogenation of pyrene with a sulfided (H_2S/H_2) iron-pillared clay catalyst at 350°C for 3 hr gave an 88% conversion to hydrogenated pyrenes. The hydropyrene yields were better than those obtained with sulfided nickel molybdenum under identical conditions (69%). Conversion to the hexahydropyrenes had not proceeded very far in the latter case. A mixed metal-pillared catalyst was tested with pyrene at 400°C in the rocking microreactor with 1000 psi of hydrogen (measured at room temperature). A 68% conversion of the pyrene was obtained. The lower yield is consistent with the smaller equilibrium constant for hydrogenation at the higher temperature. Importantly, hydrocracking of the hydrogenated pyrenes was observed (20%) at the higher temperature. At 440°C, the conversion of pyrene dropped to 50%, and the yield of hydrocracked products increased slightly (23%).

Preliminary liquefaction testing with Wyodak subbituminous coal in tetralin solvent was performed using the discreet alumina/iron-pillared catalyst. The liquefaction reaction was carried out at 425°C for 1 hr in a 71-ml reactor with 1000 psi hydrogen (measured at ambient temperature). The catalyst was sulfided by adding a small amount of carbon disulfide. THF insolubles, THF solubles, and toluene solubles were measured by weighing. The pentane solubles consisted of coal-derived oil as well as tetralin solvent; therefore, the oil yield was determined by the difference between the isolatable products described above and the maf coal weight (thus the amount includes gases and reaction product water). For this reaction, yields of THF solubles were 19%, toluene solubles were 25%,

and oils/gases were 46%, with a total conversion to soluble products of 90%. The composition of the oil product was determined by gas chromatography of the pentane/tetralin solution. This analysis showed that the coal-derived oil product consisted of 9% phenolics and 25% hydrocarbons, based on maf coal. This product quality is better than previously attained with this coal in a 1-hr single-stage run. Further coal liquefaction tests are in progress.

ACKNOWLEDGEMENT

The support of the US Department of Energy is gratefully acknowledged.

REFERENCES

1. Ryland, L.B.; Tamale, M.W.; Wilson, J.N. Catalysis; Emmett, P.H. Ed.; Reinhold: New York, 1960, Vol. 7, Chap. 1.
2. Yamanaka, S.; Doi, T.; Sako, S.; Hattori, M. Mat. Res. Bull. 1984, 19, 161-168.
3. Lee, W.Y.; Raythatha, R.H; Tatarchuk, B.J. J. Catal. 1989, 115, 159-179.