

HYDROCRACKING WITH NEW SOLID ACID CATALYSTS:
LOW SEVERITY LIQUEFACTION PRODUCTS FROM LOW RANK COAL:

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Solid acid catalysts, prepared by supporting zinc chloride on silica gel and on acid-exchanged montmorillonite, were tested for catalytic hydrocracking of first stage liquefaction products from Wyodak subbituminous coal. Unsupported acid-exchanged montmorillonite was also tested. The reactions were carried out by heating the high molecular weight, THF-soluble, low-severity product with the supported zinc chloride catalyst in a microreactor at 400°C for three hrs with 1000 psig of hydrogen (repressurized at 1-hr intervals). These reactions gave good yields of distillates (53-68%), which exceeded those obtained with conventional hydrotreating catalysts under similar conditions. Coking or retrograde condensation reactions were minimal. The distillate compositions, determined by GC/FTIR/MS/AED, consisted of phenolics, one and two ring aromatics and hydroaromatics, and alkanes. The nonvolatiles were examined by elemental analysis, FTIR, NMR, and m.w. determinations by GPC and LALLS. The hydrotreated liquefaction products, both volatiles and nonvolatiles, showed a complete absence of organo sulfur compounds, as determined by the very sensitive helium afterglow discharge emission and elemental analysis.

Key words: Liquefaction, hydrocracking, solid acid catalyst

INTRODUCTION

The preparation of new catalysts for the production of a distillate with a low content of heteroatoms such as sulfur, oxygen, and nitrogen is a major goal in coal liquefaction. More than 50 years ago Eugene Houdry (1) reported that acid modified smectites can produce gasoline in high yields when used as petroleum cracking catalysts. In contrast to thermal cracking, catalytic cracking produces gasoline of higher octane rating (2). Many cracking catalysts are combinations of alumina and silica oxides, known to exhibit acidic properties (3). The mechanism of the acid-catalyzed cracking reactions is understood to involve carbonium ion intermediates (4). The catalytic cracking of cumene has been extensively used to characterize the acidity of various catalysts (5). Synthetic silica alumina catalysts or zeolites were more stable both structurally and catalytically, gave superior product distributions compared to naturally occurring clays, and, thus revolutionized the catalytic cracking (6-10).

Petroleum hydrocracking catalysts are not necessarily effective for coal liquefaction, however. Highly acidic catalysts may result in coking on the catalyst as well as in the equipment. Although molten zinc chloride effectively depolymerizes coals (11,12), significant hydrodesulfurization of aryl sulfur compounds is not affected by this reagent (13). Other disadvantages of zinc chloride are its difficulty of recovery and corrosive nature.

In a recent paper we reported a solid acid catalyst prepared by supporting zinc chloride on silica gel to be effective in hydrodesulfurization of diphenyl sulfide and dibenzothiophene (14). The preparation and characterization of three solid acid catalysts: 1) supporting zinc chloride on silica gel, 2) supporting zinc chloride on acid-exchanged montmorillonite, and 3) unsupported acid-exchanged montmorillonite have already been reported (14,15). In this paper, we report the catalytic

hydrotreatment of the first stage products from the low-severity liquefaction of Wyodak subbituminous coal with zinc chloride supported on silica gel and on acid-exchanged montmorillonite, unsupported acid-exchanged montmorillonite, and commercial Trilobe 60 HDN catalyst.

EXPERIMENTAL

Zinc chloride on silica gel, zinc chloride on acid-exchanged montmorillonite, and unsupported acid-exchanged montmorillonite catalysts were prepared as described earlier (14,15). Total acidity and pKa's of the solid acid catalysts were determined by *n*-butyl amine titrations using Hammett indicators (16).

Analytical procedures; instrumentation:

Carbon, hydrogen, and nitrogen analyses were performed on Control Equipment Corporation Model 240XA Elemental Analyzer. Total sulfur was determined with a LECO Model 532 Sulfur Analyzer using ASTM D1551 method. Oxygen was determined by difference. The method of Vogel (17) was used for chlorine analysis.

¹³C NMR, CP/MAS solid state spectra were recorded on a Varian XL200 NMR spectrometer with Doty Scientific solids probe operating at 50.3 MHz. Infrared spectra were obtained in KBr on either a Perkin-Elmer Model 283 spectrophotometer or a Nicolet 205XB FTIR spectrometer equipped with a mercury cadmium telluride (MCTA) detector and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Quantitative GC/FID analyses were performed with a Hewlett-Packard 5880A gas chromatograph equipped with J&W 60 m x 0.25 mm (i.d.), 1.0 micron DB-1701 capillary column. *n*-Octadecane was used as the internal standard. Isotope dilution GC/MS were performed on a Finnigan 800 ITD ion trap detector with an HP-5890A gas chromatograph and a J&W 30 m x 0.32 mm (i.d.), 1.0 micron film of DB-5. Phenol, tetralin, and naphthalene were determined with the per-deuterated analogs as the respective internal standards. A 15 m x 0.25 mm (i.d.) 0.25 micron DB-5 column was used for the analysis of high boiling components. Quantitative analysis of organo sulfur compounds in the distillate was done by GC/AED.

Low severity liquefaction:

A slurry consisting of 904.5 g Wyodak coal (as received) and 1254.9 g of solvent (tetralin) was placed in a two-gallon reactor, and the reactor was sealed. The reactor was evacuated and charged with a mixture of 900 psig carbon monoxide and 100 psig hydrogen sulfide. The reactor was slowly heated to 384°C, and left at this temperature for one hour. At the end of the reaction, the reactor was cooled to room temperature, and the gases collected in a gas bag. The product slurry was separated into THF-soluble and insoluble fractions by extracting with THF. The THF-insoluble fraction was dried in vacuo at 110°C overnight, and weighed.

Preparation of solvent free low-severity product (LS-W) for second stage catalytic hydrotreatment :

A large batch of THF-soluble fraction was distilled under reduced pressure (2 torr) to remove solvents. The residue, a viscous oil, solidified upon cooling to room temperature (LS-W) was used for catalytic hydrotreatment. This product was analyzed by elemental analysis and the results are given in Table 1.

Catalytic hydrotreatment of LS-W:

In a typical run 1.0 g of LS-W and 0.50 g of the desired catalyst were placed in a tubing bomb (12-ml microreactor). The microreactor was evacuated and pressurized

with 1000 psig of hydrogen, and placed in a rocking autoclave heated to 400°C. The heating continued for three hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened.

The tubing bomb was attached to a set of three pre-weighed traps cooled in air, dry ice-acetone, and liquid nitrogen. The tubing bomb was slowly heated (3°C/min.) to 250°C, and heating was continued until distillation stopped. The distillate was weighed and dissolved in 10 ml of methylene chloride. The distillate was mixed with appropriate internal standards and analyzed by GC/FID and GC/FTIR/MS/AED. The undistilled residue was separated into THF-soluble and insoluble fractions by extracting with THF. These fractions were dried in vacuo and weighed. The mass balance data are given in Table 2.

In a separate reaction, the tubing bomb was depressurized and repressurized with 1000 psig of hydrogen at one hour intervals. The total heating time was three hours.

RESULTS AND DISCUSSION

Catalytic hydrotreating; Liquefaction:

Catalytic hydrotreating of LS-W with silica gel zinc chloride (SZC):

Hydrotreating of solvent free low severity liquefaction product from Wyodak coal (LS-W) was carried out to determine the catalytic activities of supported zinc chloride catalysts. The three-hour tests were performed with an initial (cold) hydrogen pressure of 1000 psig, which increased to 3000 psig at the final reactor temperature of 400°C. In one test, the microreactor was cooled and repressurized with hydrogen (1000 psig) after each hour, while in another test, no additional hydrogen was added over the three-hour experiment. In calculating the conversions for the reaction, it is necessary to consider that the low-severity starting material for the test consisted mostly of high molecular weight material, but did contain a small amount of tetralin and naphthalene derived from solvent used in the low severity liquefaction and a small amount of volatile coal-derived material. The yields in the hydrotreating tests were determined by measuring the amount of vacuum distillate and corrected by subtraction of the distillable material present in LS-W (20%) to obtain the actual yield.

The hydrotreatment of LS-W with silica gel-zinc chloride catalyst (SZC) in the three hour test without depressurizing and repressurizing with hydrogen gave a distillate yield of 35%. Subtraction of the LS-W volatiles resulted in an actual yield for the hydrotreating step of 15%. The most striking aspect of the composition of the distillate is the complete absence of sulfur containing compounds, as determined by the very sensitive helium afterglow discharge atomic emission detection. The GC/FTIR/MS data indicated that benzene, alkylbenzenes, cyclohexane, phenolics, tetralin, naphthalene, and a series of alkanes were the major components of the distillate.

The residue from the distillation was separated into THF-soluble and insoluble fractions. The THF-soluble fraction amounted to 54% of the weight of the starting material. This material had a hydrogen-to-carbon ratio of 1.01, identical to the starting LS-W product. ¹³C NMR, CP/MAS spectrum shows a large increase in the hydroaromatic bond at 30 ppm. This data also indicates removal of phenolics, carboxylic acids and carboxylate groups during hydrotreating. Infrared spectrum shows a larger aromatic ring absorption at 1600 cm⁻¹, which may have resulted from a change in the type of aromatic groups present. An increased aromatic content could have resulted from either cleavage and loss of alkyl groups to the distillate fraction or from condensation, dehydration, and dehydrogenation reactions to give

TABLE 1
ELEMENTAL ANALYSES OF COAL LIQUEFACTION PRODUCTS

Catalyst	Produce	C	H	N	S	O	H/C
None	Wyodak (maf)	70.9	5.2	0.9	0.6	22.3	0.88
None	LS-W	82.9	6.9	1.1	0.71	8.3	1.00
*SZC	THF-S THF-I Dist.	87.3	7.35	0.68	0.14 0.84 0.0	4.53	1.01
SZC	THF-S THF-I Dist.	88.0	6.02	1.07	0.0 0.74 0.0	4.91	0.82
AM	THF-S THF-I Dist.	83.7	5.58	1.24	0.42 0.0	9.48**	0.80
AMSZC-B	THF-S THF-I Dist.	85.4	6.38	0.94	0.0 1.47 0.0	7.28	0.90

• Single H₂ pressurization
** Includes sulfur

TABLE 2
CATALYTIC HYDROTREATING OF LS-W

CATALYST	LS-W (g)	PRODUCTS (%)		
		THF-I	THF-S	Distillate
*SZC	1.02	11.8	54.0	35.0
SZC	1.00	1.9	28.6	67.7
AM	1.00	20.0	46.0	28.0
AMZC-A	1.00	--	49.0	53.0
AMZC-B	1.00	--	41.0	62.0
HDN	1.00	14.3	49.61	35.0

• Single H₂ Pressurization

more aromatic structures. Experience with model compound hydrotreating with this catalyst (14) suggests that single rings are not hydrogenated, but naphthalenes, and polynuclear aromatics are readily hydrogenated (19). Thus the hydrotreating at 400°C appears to consist mainly of hydrocracking alkylaromatics and hydrogenation of multi-ring aromatics. Hydrotreating may predominate over hydrogenation, because of the higher concentration of single ring aromatics in the low-rank coals.

The THF-insoluble fraction from the experiment without repressurization consisted mainly of catalyst, but did contain organic material amounting to 12% of the starting LS-W. This material was also more aromatic than the original LS-W.

The hydrotreating of LS-W with silica gel-zinc chloride catalyst with repressurization of hydrogen at one-hour intervals gave a distillate yield of 68% (actual 48%). The composition of the distillate was similar to that of the product from the single pressurization with hydrogen. The THF-soluble fraction amounted to 24% of the starting material. As in the experiment discussed above, the infrared spectrum indicated this fraction to be more aromatic than the original LS-W. The THF-soluble fraction was essentially the recovered catalyst with only a small amount (<3%) of carbonaceous material.

Catalytic hydrotreating with montmorillonite-zinc chloride (AMZC):

Catalytic hydrotreating of LS-W with acid-exchanged montmorillonite (AM) and hydrogen depressurizing and repressurizing at one-hour intervals gave 28% distillate. Since, 20% distillate was already present in the LS-W, only 8% of the distillate was actually produced during the second stage of the reaction. The GC/MS data indicated the major components of the distillate to be tetralin, naphthalene, and phenols. Tetralin is more likely to be solvent-derived and naphthalene could either be solvent-derived, coal-derived or both. Other products in the distillate were cresols, benzene, alkylbenzenes, and alkylnaphthalenes. A significant portion of the starting material (20%) became insoluble in THF after the second stage reaction, which may be due to condensation reactions catalyzed by the acidity of the clay.

Catalytic hydrotreating with zinc chloride supported on acid-exchanged montmorillonite prepared from clay dried at 110°C in vacuo (AMZC-A) gave 53% distillate (actual 33%). The stability and catalytic activity of the catalyst was found to depend on the drying temperature of the clay. The zinc chloride supported catalyst that was prepared from clay dried at 250°C (AMZC-B), was not only more stable on long standing but also gave higher distillate yield, 62% (42% actual). The distillate yield with this catalyst was comparable to that obtained from silica gel-zinc chloride catalyst. Furthermore, no coking or enhanced aromatic residue was formed during catalytic upgrading.

Catalytic hydrotreatment with commercial Ni-Mo catalyst (HDN):

In order to evaluate the catalytic activity of the zinc chloride supported silica gel and acid-exchanged montmorillonite, reaction of low severity Wyodak (LS-W) product with commercially available HDN catalyst was carried out under the same conditions as described above, and the results compared. The distillate yield was only 35% (actual 15%), which is significantly lower than those obtained with zinc chloride supported on silica gel and acid-exchanged montmorillonite. The product distribution of the distillate was much the same as with supported zinc chloride catalysts. The THF-soluble fraction was 50% of the starting material. A significant amount of organic material became insoluble in THF, which may have been formed due to dealkylation or condensation reactions (15).

Catalytic hydrotreating: Desulfurization:

Table 3 shows the sulfur removal for four different catalysts. The distillates obtained from these reactions did not contain any sulfur as indicated by very sensitive helium afterglow atomic emission spectroscopy. Therefore, sulfur amounts in the recovered catalyst (THF-insolubles) and THF-soluble fraction were used to determine desulfurization during catalytic hydrotreating of LS-W. Elemental analysis of the THF-insoluble fraction gave 0.74% sulfur (0.0075 g S). This amount of sulfur is essentially the same as that present in the starting LS-W (0.0071 g). These data demonstrate that the catalyst is highly effective in removing sulfur from the bottoms as well as the distillate. The occurrence of zinc sulfide in the catalyst is expected (14) but has not yet been confirmed. However, only 73.6% sulfur was removed from LS-W in the test without hydrogen repressurization. These results suggest that hydrogen repressurization is needed for the efficient removal of organic sulfur from coal products. Acid-exchanged montmorillonite removed only 42.3% sulfur from LS-W. However, on supporting zinc chloride on acid-exchanged montmorillonite, the desulfurization activity of the clay was considerably increased.

TABLE 3
SULFUR BALANCE

Catalyst	S(g)				% S Removed
	Reactant	Products			
	LS-W	Distillate	THF-S	Recovered Catalyst	
*SZC	0.0072	0.0	--	0.0053	73.6
SZC	0.0071	0.0	0.0	0.0074	100
AM	0.0071	0.0	--	0.0030	42.3
AMZC-B	0.0071	0.0	0.0007	0.0060	84.5

* Single H₂ Pressurization

CONCLUSIONS

Comparing the results of hydrocracking of low-severity liquefaction Wyodak products with supported zinc chloride catalysts to the results with HDN catalyst shows that these supported catalysts give higher distillate yields and effectively remove organic sulfur under mild conditions. The strong acid hydrotreating catalyst (acid-exchanged montmorillonite) was not very effective in hydrotreating. The experiments showed that repressurizing the hydrogen is needed to sustain hydrogenation and prevent condensations at this temperature. These acid catalysts are effective in removing organic sulfur from coal-derived products.

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