

MOLTEN SALT CATALYSTS FOR HYDROCRACKING OF POLYNUCLEAR HYDROCARBONS

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INTRODUCTION

Intensive investigation has been underway for some time in the laboratories of Consolidation Coal Co. of various catalytic systems for the hydrocracking of coal "extract" to distillate oils. The extraction process and its integration with subsequent hydrocracking operations is described in several recent patents.⁽⁸⁾

Contact catalysts for hydrocracking of the extract have been extensively investigated in our laboratories both in batch and in small continuous hydrocracking units. The hydrocracking of coal extract using a contact catalyst in a three-phase fluidized system will be demonstrated on a 50 barrel/day pilot plant now being constructed at Cresap, W. Va.

Sulfur-resistant catalysts of the hydrofining type have given the most satisfactory results. These usually comprise a combination of the sulfides of Mo, Ni and Co on alumina gel support. Best results are obtained with large-pore alumina supports.

Rapid and efficient hydrogenolysis of the coal extract is effected at temperatures in the range of 800-825°F and at conversion levels up to about 60%.

The hydrogenated non-distillable residue from this operation, however, is much more refractory than the feed extract, and can be converted at practical rates only by raising the operating temperature. Although this is practical to do, the yield of the more valuable liquid products is lowered since the gas yield rises with increasing operating temperatures.

The limiting kinetic factor in the use of the "hydrofining" type catalyst is their very low cracking activity.

Dual function contact catalysts promoted by the use of acidic cracking agents were investigated to determine if they would be useful in conversion of the hydro residue. As the work to be reported below shows, this type of catalyst does not actually give improved performance since the acid sites are rapidly poisoned by the nitrogen content of the feed.

Attention was therefore turned to the development of a fused metal halide catalyst system.

The use of massive quantities of the catalyst was found to be desirable not only to develop the maximum hydrocracking activity but to "overwhelm" any nitrogen poisons in the feedstock. Fused salts were emphasized since the process under development visualizes continuous circulation of melt between hydrocracking and a regeneration operation where the nitrogen poisons would be removed.

The development of the massive fused salt catalyst system was initiated by a study of their activity in comparison with contact catalysts in the hydrocracking of hydro residue and a model polynuclear hydrocarbon: pyrene.

A voluminous literature exists on the use of metal halide catalysts in the hydrocracking of coal and coal tar. In many cases, the metal halide was not introduced directly as such but in all likelihood was generated in part in situ by reaction of a halogen promoter with the free metal or with a metal salt.

Excellent review articles^(17,18) and books^(8,11) are available summarizing this work so that there is no need to extensively discuss the original references.

In all of this work relatively small amounts of catalyst, i.e., less than 5 wt. % of the feed and generally of the order of 1 wt. % or less were employed. Under these conditions most investigators^(13,14,20) agree that halogen promoted tin catalysts are the most active of this class. The superiority of tin catalysts over zinc catalysts when used in small concentrations is further illustrated by the fact that there have been no commercial coal hydrogenation operations using zinc catalyst while there were commercial operations in both England^(4,7) and Germany⁽¹¹⁾ which used tin catalysts.

In addition, excellent results equal or superior to those with $ZnCl_2$ have been obtained with 1% nickelous chloride⁽¹⁹⁾ catalyst when proper methods of distribution of the catalyst on the substrate were used.

The above order of activity has no relationship to the cracking activity of these catalysts. Zinc chloride is well known as a Lewis acid type catalyst⁽³⁾ which has fairly good catalytic activity for most Friedel Crafts type reactions such as polymerization of olefins, alkylation of aromatic compounds with olefins, etc. It also is well known as a cracking catalyst and has been used, for example, for the catalytic cracking of shale oil.⁽⁶⁾

Stannous chloride, however, is not well known as an active Lewis acid although it does have electron accepting properties as evidenced by its formation of ammoniate complexes such as $SnCl_2 \cdot NH_3$. It is reported to have some catalytic activity of the Friedel Crafts type for reactions such as the polymerization of certain unsaturated compounds such as vinyl ethers,⁽¹²⁾ and the acetylation of olefins, i.e., reaction of acetic anhydride with 2,4,4-trimethyl pentene-1.⁽¹⁾ However, in general, it must be regarded as a very weak Friedel Crafts type catalyst with very little cracking activity as compared with $ZnCl_2$.

There is little or no evidence likewise that nickelous chloride has any substantial cracking or Friedel Crafts activity.

Weller⁽¹⁸⁾ has pointed out that there is sufficient sulfur in most of the feedstocks to decompose the metal halides, in the small quantities used, by the reaction



and therefore concludes that the halide is not the true catalyst. Rather he proposes that the catalyst is really a dual function one in that the HCl is a splitting or cracking catalyst while the tin acts as a hydrogenating component to stabilize the reactive fragments by reaction with hydrogen. In this respect, the point of view is quite similar to the commonly accepted mechanism of the action of dual function contact catalysts used for hydrocracking of petroleum feedstocks. In this latter case, the role of the hydrogenating metal is regarded⁽¹³⁾ as one of prevention of coke deposits by hydrogenation of highly unsaturated intermediates formed by catalytic cracking on the acid sites of the catalyst.

The above theory in the case of tin, however, is difficult to accept since there are no experimental facts with pure organic compounds which show that either tin metal or tin sulfide per se has any substantial hydrogenating activity.

It may be, as a matter of fact, that the unique position of tin chloride in the hydrogenolysis of coal is due to its known better thermodynamic stability towards decomposition by hydrogen sulfide as compared with zinc chloride, for example,

Equilibrium constants at 700°K for reaction (1) of SnCl₂ and ZnCl₂ with H₂S were calculated from available thermodynamic data with the results shown below:

$$K_M = \frac{P_{HCl}^2}{P_{H_2S}} \quad K_{Zn} = 400 \quad K_{Sn} = 1.5$$

It is thus clear that tin chloride is much more stable than zinc chloride and that under equivalent operating conditions with the same quantity of promoter, etc., that a much higher percentage of the tin will be present as tin chloride.

Thus, it appears possible that in contradistinction to the opinion expressed by Weller,⁽¹⁸⁾ the true catalyst is the small amount of undecomposed metal halide and that no dual function catalysis is involved.

Another object of the present investigation therefore was to obtain a better understanding of the catalytic activity of molten metal halides in hydrocracking processes. A pure compound, i.e., pyrene, was used to eliminate complications due to the interaction of the metal halide with hetero atom impurities and also to simplify analytical interpretation of the results. Massive quantities were used to insure the presence of a definite molten halide phase and because of the greater catalytic activity when massive quantities are used.

One of the points that was felt desirable to clarify was to what extent satisfactory operation and activation of hydrogen could be achieved with a molten halide catalyst without the addition of a separate hydrogenating component. The prior hydrocracking literature is not wholly clear on this point. There are, however, some references which showed that AlCl₃ and FeCl₃⁽¹⁰⁾ have definite catalytic activity for the hydrocracking of naphthalene. Only a small percent of catalyst was used such that no molten halide was likely present and rather severe conditions, i.e., 460°C for 3 hours were employed. Sixty percent conversion to single ring aromatic hydrocarbons was reported.

Similar results were obtained with anthracene although a lower yield of low boiling aromatics was obtained.

Winter and Free⁽²¹⁾ subsequently investigated the hydrocracking of naphthalene, anthracene and phenanthrene with FeCl₃ and AlCl₃ catalysts at hydrogen pressures of 190-250 atms. and temperatures in the range of 350-490°C. They observed the formation of significant quantities of pitchy condensation products as well as lower boiling aromatic liquids. Again, small quantities of catalyst were used.

Another pertinent reference is that of Schmerling and Ipatieff⁽¹⁶⁾ who showed that aqueous zinc chloride impregnated on alumina was an active catalyst for the hydrocracking of naphthalene.

Materials Used

Pyrene - Obtained from Gesellschaft Fur Teerverwertung MBH, m.p. = 149-151°C, b.p. = 393.5°C, purity = 98%. Typical analysis of the feedstock is shown in Table I.

Hydro Residue - The hydro residue used for runs in Table III was produced by hydrocracking a coal extract in a continuous fluidized bed unit using a nickel molybdate catalyst described below. The residue represents 29% of the extract fed and is free of material boiling below 400°C. The extract was obtained by extracting a high volatile bituminous coal from the Pittsburgh Seam, Ireland Mine, with tetralin, and amounted to 57% of the moisture- and ash-free coal. Some properties of the hydro residue are given in Table I.

Benzene - Fischer Scientific Co. Certified Reagent, Thiophene-free.

Catalysts

1. Nickel Molybdate on Alumina - A commercial hydrofining catalyst, containing 6.8% molybdenum, 3.8% nickel, and 0.1% cobalt supported on alumina gel. Unless otherwise noted, this catalyst was presulfided with 15% H₂S - 85% H₂ at 500°F. It has a surface area of 200 m²/g, a porosity of 77%, and an average pore diameter of 200 Å.
2. Fluorided Nickel Molybdate on Alumina - The above sulfided catalyst which was treated with 4 mole percent HF in nitrogen at 300°C until it consumed HF corresponding to 10% of its weight.
3. Nickel Molybdate on Silica-Alumina - Active metals corresponding to those in Catalyst No. 1 (6.8% Mo, 3.8% Ni, and 0.1% Co) were locally impregnated on Houdry S-90, a 12.5% alumina cracking catalyst with a surface area of 430 m²/g, a porosity of 65%, and an average pore diameter of 70 Å.
4. Zinc Chloride - Fisher Scientific Co. Certified Reagent, various lots 96.2 to 98.8% pure, dried before use by heating in a vacuum at 110°C. After this treatment, it contained 1 to 1.5% water and up to 1.8% ZnO.
5. Stannous Chloride - Fisher Scientific Co. Certified Reagent, SnCl₂·2 H₂O, heated before use at 150°C and 1 mm Hg pressure for 2 hours to remove water.
6. Aluminum Bromide - Fisher Scientific Co. Certified Reagent, Anhydrous, 99% pure.
7. Nickel Molybdate Catalyst Impregnated with Zinc Chloride - A solution of zinc chloride in methyl ethyl ketone was used to impregnate Catalyst No. 1, following the procedure used by Innes for determining catalyst porosity.⁽⁸⁾ The solvent was removed by heating at 60°C and atmospheric pressure overnight, followed by two hours at 200°C and 1 mm Hg pressure. The final catalyst contained 19% zinc chloride.
8. Zinc Chloride on Alumina - American Cyanamid gamma alumina stabilized with 2% silica was impregnated with 19% zinc chloride by the same procedure as for Catalyst No. 7. The alumina had a surface area of over 225 m²/g, and an average pore diameter of 80-100 Å.
9. Mixtures - Runs 2 and 3 were made with mixtures of Catalyst No. 1 and a salt catalyst. These were added separately to the autoclave.

Equipment

The basic unit for the hydrocracking tests was an American Instrument Co., Catalog No. 40-2150 rocking autoclave. The normal rocking motion of 36 cycles/sec. about the axis of the autoclave was found to give good catalyst mixing only if the catalyst was 35x65 mesh or finer. In order to test catalysts of 1/16-inch diameter such as were being used on continuous units, the autoclave and furnace were mounted on the end of a 12-inch arm, so that a shaking motion resulted rather than rocking. The autoclave was driven at 86 cycles/sec. through an angle of 30° at the end of the 12-inch lever arm as shown in Figure No. 1.

Other features of the test unit are evident from Figure No. 1. Hydrogen can be frequently added to the autoclave during the run to maintain pressure. Hydrogen consumption is measured directly by the change in pressure on the 300 ml accumulator. The accumulator is isolated from the compressor during a run and a precision Heise gauge indicates the pressure to ± 10 psi.

Procedure for Hydrocracking Tests

The 300 ml autoclave is weighed and 50 grams of feed plus the required weight of catalyst added. The autoclave is then closed, evacuated through valve V-2, and pressure tested with 1000-1500 psig of hydrogen from the accumulator. Heating is then commenced with V-3 closed.

When the temperature approaches the area where reaction will begin (ca. 300°C), V-3 is opened and the reactor pressure watched for evidence of hydrogen consumption. Hydrogen is thereafter supplied as needed in frequent increments from the accumulator until the full hydrogen pressure is reached when reaction temperature is reached. Thereafter, pressure is maintained, if necessary, by more hydrogen additions. The rate of temperature rise is controlled to average 10°C/min. to 375°C. From 375°C to the maximum temperature requires 5 to 15 minutes depending upon the temperature used and the extent of the exothermic reaction obtained. The temperature is then held at the desired level for a set time (usually one hour), and then lowered rapidly to 250°C via an air blast. After reaching 250°C, the motion is stopped, valve V-3 is closed, and the temperature maintained during depressuring of the lines. The line from the accumulator to the autoclave is disconnected at V-3 and replaced with the line (dashed) to the recovery train. The train is evacuated through V-4, and the contents bled off through a dry-ice-acetone cold trap, an Ascarite trap to remove acid gases, and into a gas holder.

Analysis of Hydrocracked Products from Runs Using Zinc Chloride

The gases passing through the cold trap from the 250°C bleed-off are metered and analyzed on a molecular sieve gas chromatograph column (Linde 5A, Medium Grade). The hydrogen gas remaining after the run is subtracted from that fed from the accumulator to give the overall hydrogen consumption for the run. The volatile materials in the cold trap are bled into an evacuated bottle by placing the cold trap in ice water until the sample bottle reaches 1 atm. The cold trap is then connected to an evacuated stainless steel bomb immersed in dry-ice-acetone and the original trap allowed to rise to room temperature. The volatile products collected in the glass sample bottle and the stainless bomb are subsequently analyzed for C₁ to C₇ hydrocarbons on a gas chromatograph (hexamethylphosphoramide supported on Chromosorb W). The light oil and water remaining in the original cold trap are separated and analyzed.

The product remaining in the autoclave at 250°C is removed after cooling to room temperature, using a mixture of organic solvent (carbon disulfide for pyrene runs, benzene for extract hydro residue runs) and water. The residue is repeatedly washed with water in a Waring Blender and filtered until free of chloride ion. The filtrates are separated into water and organic phases and each washed until water is free of organics and the organic phase free of chloride.

The filter cake from the final water wash is Soxhlet extracted with methyl ethyl ketone (MEK). The soluble fraction is combined with the organic filtrate phase and distilled.

The MEK-Insoluble material in the Soxhlet thimble includes zinc oxide and zinc sulfide as well as organic residue. The amounts of each are determined by analysis.

The procedures for tin chloride or combined catalyst runs followed the above format with very minor modifications. Where only a supported catalyst was involved, the procedure simplified to pressure filtration (20 psi), MEK extraction of the catalyst and sampling of the filtrates.

Product Boiling Range

Boiling ranges of the pyrene products were determined by gas chromatography using a silicone rubber column at 170°C with flame ionization detector. This permitted CS₂ to be used as a solvent for solid fractions without interference. A fairly simple pattern of about 20 peaks resulted.

Products from runs in which hydro residue was fed were vacuum distilled to give the distillate distribution because of the more complicated nature of the feed.

Hydrogen consumption is determined directly from hydrogen fed and recovered. Conversion is calculated by subtracting the recovered residue (+400°C) from the weight of feed and dividing the difference by the weight of feed.

A measure of the asphaltic nature of extracts and hydro residue (Table I) is given by solvent fractionation. "Benzene-Insolubles" is the fraction of extract insoluble in benzene at its atmospheric boiling point (Soxhlet apparatus). "Asphaltenes" is the benzene-soluble, cyclohexane-insoluble fraction, determined by mixing one part of benzene-soluble material with nine parts of benzene and 100 parts of cyclohexane, by weight, and filtering at room temperature. The fraction soluble in this mixture is termed "oil".

RESULTS AND DISCUSSION

Contact Catalysts with Cracking Promoters

The first approach used in attempting to enhance the cracking activity of the contact-type catalyst was to add cracking promoters. One method used was to incorporate the promoters in the contact-type catalysts either by impregnation with zinc chloride or by fluorination in the vapor phase with anhydrous hydrofluoric acid. Another method employed was to impregnate the hydrogenating metals on an active silica-alumina cracking catalyst base. Still another method was investigated in which the cracking catalyst, i.e., zinc chloride was not impregnated on the support but was simply added as a separate component to the autoclave. Finally, the use of a cracking catalyst by itself, i.e., zinc chloride impregnated on γ - Al_2O_3 was investigated without the addition of hydrogenating metals. The activity tests with pyrene feedstock are summarized in Table II. All runs were carried out at standardized conditions, i.e., a total hot pressure of 4200 psig and 1 hour residence time at the operating temperature of 427°C.

Runs 2 and 5 contained the same quantity of zinc chloride in each case, the only difference being that in the former case the zinc chloride was added as a separate component while in the latter case it was first impregnated on the nickel molybdate catalyst.

No detailed structural investigation was made of the products of the reaction. The boiling ranges of Table II, however, correspond roughly to the following classes of compounds as given below:

340 x 390°C	Partially Hydrogenated Pyrenes
280 x 340°C	Alkylated and Partially Hydrogenated Phenanthrenes
200 x 280°C	Alkylated and Partially Hydrogenated Naphthalenes
C_5 x 200°C	Alkyl Benzenes, Single Ring Naphthenes and Paraffins

In interpreting results, it should be noted that the hydrocracked product consists only of products boiling below 340°C. The pyrene is very readily hydrogenated such that in almost all cases very little remains completely unconverted.

In almost all cases an increase in hydrocracking activity was obtained by addition of the cracking promoter. This is evidenced by an increase in the yield of C_5 x 340°C distillate products as well as a substantial increase in the hydrogen consumption. A lone exception was stannous chloride. Here, the very low cracking activity of the metal halide was more than compensated for by a decreased activity of the contact catalyst. The latter may be due to coating of the contact catalyst with the molten salt. Zinc chloride, however, is such a strong cracking catalyst that it acts as a net promoter in spite of the fact that the same type of deactivation by coating of the

contact catalyst is possible here too. As a matter of fact, it appears to be slightly more active when added separately than when it is impregnated on the catalyst before use.

It is interesting to note that $ZnCl_2$ on Al_2O_3 , even without the hydrogenating metals, has hydrocracking activity although it is less than that of the nickel molybdate catalyst by itself. It also shows a relatively high coke yield which may possibly be attributed to the absence of hydrogenating metals. It is clear, however, as was shown by Schmerling and Ipatieff,⁽¹⁶⁾ that zinc chloride even in the absence of hydrogenating metals is capable of activating hydrogen for the hydrogenation and hydrocracking of polynuclear aromatic hydrocarbons.

The activities of the other two "dual function catalysts" investigated, i.e., fluorided nickel molybdate and Co-Mo-Ni on a cracking catalyst base (Houdry S-90) are also higher than that of the nickel molybdate catalyst and are even slightly more active than the zinc chloride promoted catalysts for total conversion. They produce, however, more middle range boiling distillates and less gasoline. The yield of $C_5 \times 200^\circ C$ distillate was 27.1% of the feed in the case of the zinc chloride catalyst and only 13.5% of the feed for the S-90 catalyst.

Ammonia Tolerance of Promoted Catalysts

The development of the dual function catalysts was aimed at their use, as mentioned above, in the hydrocracking of refractory residues from the hydrogenolysis of coal extract. These residues, as the data given in Table I show, contain substantial quantities of nitrogen of the order of 1 wt. % or more. Therefore, if these catalysts were to be of much use in such an operation, they must be relatively resistant to poisoning by NH_3 and other nitrogen bases released during the hydrocracking process.

The investigation was therefore directed towards determining the activity of these catalysts as a function of the partial pressure of NH_3 in the gas phase. In order to guide the experimental work, rough absorption isotherms for NH_3 were determined for two of the above catalysts, i.e., $ZnCl_2$ on nickel molybdate and Co-Mo-Ni on S-90. These are shown in Figure 2.

The results are at least roughly correct since the $350^\circ C$ isotherm for Catalyst No. 7 approaches the theoretical asymptotic value of 32 cc NH_3/gm . This value corresponds to the addition of 1 mole of NH_3 to 1 mole of $ZnCl_2$.

Experiments were now conducted in which controlled amounts of NH_3 were added such that the partial pressure of NH_3 could be estimated after correction for the amount absorbed on the catalyst.

The results for three types of catalysts are summarized in Figure 3 where yields of distillates are plotted as a function of NH_3 pressure. It is noted that even the nickel molybdate catalyst by itself suffers a loss of activity on addition of NH_3 . The S-90 catalyst appears to be able to tolerate somewhat larger quantities of NH_3 than the $ZnCl_2$ -impregnated catalyst probably because the acidic sites are weaker and are more readily dissociated. This fact is evident from the absorption isotherms given in Figure 2.

Thus, to obtain a substantial improvement in activity over the nickel molybdate catalyst, the NH_3 pressure must be maintained below about 5 psi for the $ZnCl_2$ promoted catalyst or slightly higher for the S-90 catalyst. To achieve such low partial pressures of NH_3 with high nitrogen feedstocks would require, in general, impractically high rates of hydrogen circulation. Consider a feedstock, for example, which releases 1 wt. % nitrogen as ammonia in a hydrocracking process wherein the hydrogen partial pressure is maintained at 200 atms. A hydrogen circulation rate of greater than 160 SCF/lb feed would be required in this case to maintain the partial pressure of NH_3 below 5 psia in the outlet gas.

Autoclave tests were run with the hydro residue itself wherein the S-90 catalyst was compared with the nickel molybdate catalyst. The results of these tests are shown in Table III. It is seen that the high nitrogen content of the feedstock as expected has poisoned the activity of the S-90 catalyst such that it is less active than the nickel molybdate.

The activity of fused zinc chloride catalyst itself with no support or other additive was tested in massive quantities on this same feedstock with the results shown in Table III. In spite of the fact that a lower temperature was used, the molten zinc chloride catalyst more than doubled the conversion and hydrogen consumption. The selectivity of the process as measured by the quantity $(C_1-C_3) \times 100/\text{conversion}$ is also improved with the molten zinc chloride catalyst. C_1-C_3 here refers to the weight percent yield of methane, ethane plus propane.

Very noteworthy, likewise, is the high selectivity of the process for production of gasoline. Ninety-one percent of the distillate oils (b.p. below 400°C) boil in the gasoline range in the case of the ZnCl_2 catalyst, and only 52 percent in the case of the nickel molybdate catalyst.

Another distinctive feature of catalysis with massive quantities of zinc chloride is the high ratio of iso paraffins to n-paraffins produced as evidenced by the ratio of isobutane to n-butane of over 6/1. This phenomenon is observed with conventional "dual function" hydrocracking catalysts when the feedstock is free of nitrogen poisons. In this case the same phenomenon is observed by "over whelming" the nitrogen poisons with an excess of catalyst.

In contradistinction runs 8 and 9 using contact catalysts show a low ratio of iso to n-butane indicating that the acid cracking sites have been poisoned by the nitrogen bases in the feedstock.

These results point to the clear superiority of massive zinc chloride melts as a hydrocracking catalyst. The development is proceeding with the central concept of continuously circulating the molten halide catalyst to a regeneration step where the nitrogen poisons would be removed. Data on the effect of basic nitrogen on catalyst activity will be given in a subsequent paper.

Activity Tests of Molten Halide Catalysts with Pyrene Feedstock

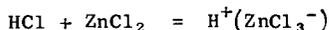
A series of further tests were made with pyrene feedstock to provide more background information for development of the molten halide catalyst system. Experiments were conducted to further clarify the effect of the quantity of catalyst used, the effect of the addition of cracking and hydrogenation promoters as well as a comparison of the activity of fused zinc chloride with other molten halide salts. The experimental results are summarized in Table IV.

It is noted that when the zinc chloride catalyst is used in relatively small amounts (in 7 percent by weight of the pyrene feed, Run 11), that the activity is quite low. The main reaction appears to be hydrogenation of pyrene to partially hydrogenated pyrenes with some hydrocracking to light distillates. The extent of hydrocracking is also much less than when the same amount of zinc chloride is used dispersed on an alumina support (cf. Run 7, Table II). However, when massive quantities of zinc chloride melt are used, i.e., Run 12, the hydrocracking of pyrene proceeds very vigorously. A much greater degree of hydrocracking is obtained than with any of the promoted contact catalysts discussed above. The result is also quite similar to that observed when massive quantities of zinc chloride melt were used for hydrocracking of extract residue (cf. Run 10, Table III). The characteristic high ratio of iso to n-butane (5.6/1) and high proportion of gasoline boiling range liquid, i.e., 91%, in the total $C_5 \times 340^\circ\text{C}$ distillate is again observed.

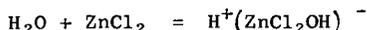
The coke plus tar yield was rather high in Run 12, i.e., 7.5% of the feed in spite of the relatively high pressure employed. Runs 13 and 14 were conducted to determine

if the addition of hydrogenating components to the melt, i.e., SnCl_2 and MoO_3 would reduce the coke plus tar yield. Stannous chloride in the small amounts used was completely inert, i.e., no difference in results is apparent between Runs 12 and 13. Molybdc oxide (Run 14) did increase the hydrogen consumption and decrease the gas yield slightly, but actually caused an increase rather than a decrease in tar plus coke yield.

Runs 15 and 16 were conducted to determine what the effect of the addition of cracking promoters to the melt would be. HCl potentially can form the unstable Friedel Crafts acid by the reaction,



while water can undergo a similar reaction,



The original melt was not completely anhydrous and usually contained about 1 wt. % H_2O . Thus, the addition of further quantities of water can increase the amount of acidic cracking catalyst by the above reaction.

It is seen that the addition of HCl is unfavorable in that it causes a large increase in the amount of coke. Water addition on the other hand increased the overall hydrogen consumption with only a slight increase in the amount of tar plus coke.

Run 17 was conducted to determine whether massive quantities of stannous chloride melt would behave similarly to zinc chloride. It is seen that it is a very weak catalyst and that practically no hydrocracking takes place. The only process observed is hydrogenation to partially hydrogenated pyrenes. It would appear that the relatively good activity of tin catalysts for hydrogenolysis of coal and coal extract must in some way be related to their activity with respect to scission of specific weak bonds that are not present in pyrene or its partially hydrogenated homologues.

Finally, one experiment (Run 18) was conducted using massive quantities of an AlBr_3 melt. Due to the very high activity of this catalyst, it was not possible to run at comparable conditions used for the ZnCl_2 catalyst. The experiment was run at a much lower temperature, i.e., 300°C ; and a lower pressure, i.e., 3000 psig. As a matter of fact the absorption of hydrogen was initially so rapid that the pressure fell considerably below 3000 psig at first. This may be the reason for the fairly high yield of tar obtained.

It is obvious, however, that AlBr_3 is a much more active catalyst than zinc chloride. The conditions chosen were too severe in that, outside of the tar produced, the feed pyrene was almost completely degraded to low molecular weight paraffins in the range of C_1 to C_6 . The $\text{C}_5 \times 150^\circ\text{C}$ distillate, as determined by gas chromatography, showed the composition given below:

	Wt. % of Cut
Isopentane	48.2
n-Pentane	18.2
2,2-Dimethyl Butane	1.8
2,3-Dimethyl Butane)	
2-Methyl Pentane)	8.2
3-Methyl Pentane	3.7
n-Hexane	2.5
Methyl Cyclopentane	0.4
$\text{C}_7 +$	18.0
Total	100.0

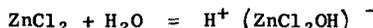
The zinc chloride catalyst is almost completely inactive for hydrocracking of single-ring aromatic hydrocarbons as the data of Table V show where benzene is used as a model compound. This is one reason that high yields of gasoline boiling range hydrocarbons are obtained with zinc chloride melt catalyst. In other words, the hydrocracking process is suspended after aromatic hydrocarbons boiling in gasoline range are produced. Other experiments showed that the whole gasoline fraction including aromatics, naphthenes and paraffins are resistant to further hydrocracking by zinc chloride catalyst.

This is not true of aluminum halide catalysts since it is clear that continued hydrocracking to produce predominantly propane and butanes occurred under the conditions used. The effect of using milder operating conditions with aluminum halide catalysts is now being investigated.

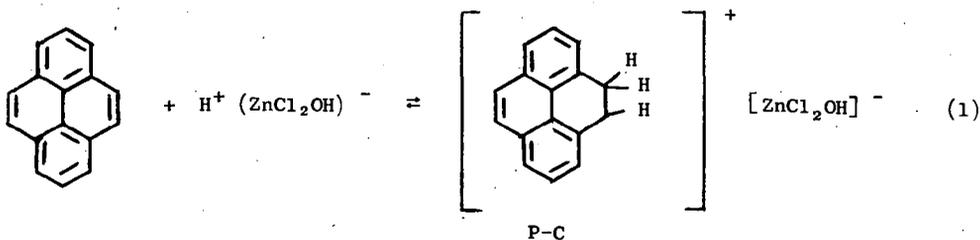
Mechanism of Hydrocracking with Molten Halide Catalysts

The investigation was not aimed at specifically unravelling the mechanism of the hydrocracking process so that one can only speculate on this question.

The nature of the active catalyst is not clear but is likely a Friedel Crafts acid. As stated above, no precautions were used to completely dehydrate the zinc chloride melts used and they usually contained about 1 wt. % of water. Thus, the active catalyst may be the acid produced by interaction of zinc chloride with water

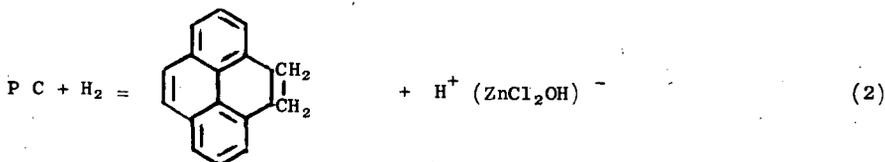


The first step in hydrocracking is likely the addition of the Friedel Crafts acid to the labile unsaturated bond between the 9 and 10 carbon atoms of the pyrene ring.



This is similar to the first step in the mechanism proposed by Schmerling⁽¹⁵⁾ and others for alkylation of isoparaffins with olefins using Friedel Crafts catalysts.

The aromatic-catalyst complex, written as P C, can then react with hydrogen to regenerate the catalyst and produce 9,10-dehydropyrene as follows:



This basic mechanism for hydrogenation can continue for further absorption of hydrogen, scission reactions leading to ring opening and dihydroalkylation, etc.

Experiments were carried out to determine the miscibility of $ZnCl_2$ and pyrene in one another. After mixing an equal weight of the two components at $350^\circ C$, no appreciable separation of phases could be detected on standing for one hour. Whether one is dealing with a true solution or relatively stable emulsions is not certain at this time.

The high dependence of reaction rate on catalyst concentration would not be surprising if one is dealing with a homogenous solution of catalyst and hydrocarbon reactant.

It is not clear at present whether the results reported here are unique to molten halide Friedel-Crafts catalysts. It is possible that similar results can be obtained with some liquid protonic acids such as phosphoric acid, hydrofluoric acid, hydroxy fluoboric acid, etc., once proper conditions are selected. Experiments are now in progress to check these possibilities. Preliminary results indicate that phosphoric acid is inactive for hydrocracking of pyrene at $300^\circ C$ and 3000 psig hot pressure.

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TABLE I

Analysis of Feedstocks

<u>Feed</u>	<u>Pyrene</u>	<u>29% Residue (+400°C) from Extract Hydrogenation</u>
H	4.94	6.82
C	94.87	90.79
N	0.02	1.17
O	0.06	1.07
S	0.11	0.15
Benzene-Insolubles	--	3
Asphaltenes	--	30
Oil	--	67

TABLE II

Comparison of Activity of Various Contact Catalysts
Effect of Promotion with Acid Cracking Catalysts

Hydrocracking of Pyrene at 427°C and 4200 psig Hot Pressure
Residence Time at Temperature = 60 min.

Run No.	1	2	3	4	5	6	7
Contact Catalyst	Sulfided Nickel Molybdate	ZnCl ₂	SnCl ₂	Fluorided Nickel Molybdate	ZnCl ₂ on Nickel Molybdate	Co-Mo-Ni on S-90	ZnCl ₂ -Al ₂ O ₃
Other Catalyst	None	ZnCl ₂	SnCl ₂	None	--	--	--
Contact Catalyst (Wt. Ratio) Pyrene	0.30	0.30	0.30	0.30	0.37	0.30	0.37
Other Catalyst (Wt. Ratio) Pyrene	0	0.07	0.07	0	--	--	--
Yields, Wt. % of Pyrene Feed							
CH ₄	0.0	0.4	0.2	0.0	0.4	0.2	0.5
C ₂ H ₆	0.3	1.3	0.8	0.2	1.2	0.6	1.4
C ₃ H ₈	0.7	1.7	1.4	0.5	1.3	1.1	1.6
C ₄ H ₁₀	0.0	0.6	0.1	0.2	0.3	0.5	0.5
C ₅ x 150°C Dist.	2.7	15.8	2.9	5.8	22.1	6.4	4.1
150 x 200°C Dist.	0.0	8.4	1.3	0.2	5.0	7.1	2.2
200 x 280°C Dist.	27.1	17.5	11.1	9.3	11.4	15.4	8.5
280 x 340°C Dist.	18.7	20.5	15.8	68.5	16.3	45.9	16.8
340 x 390°C Dist.	52.6	35.6	59.9	21.4	42.7	26.8	47.4
Pyrene	2.6	1.9	9.0	0.0	3.2	0.6	13.6
Coke on Catalyst	0.6	2.8	1.6	0.9	2.1	1.9	7.0
Total Including H Consumed	105.3	106.5	104.1	107.0	106.0	106.6	103.6
H Consumed, Wt. %	5.33	6.56	4.12	6.98	5.98	6.62	3.56

TABLE III

Comparison of Contact Catalysts with ZnCl₂ Melt for Hydrocracking of Extract Hydro Residue

Total Pressure = 4200 psig - Residence Time at Temperature = 60 min.

Run No.	8	9	10
Catalyst	Co-Mo-Ni on S-90	Sulfided Nickel Molybdate	ZnCl ₂ Melt
Temperature, °C	441	441	427
Catalyst/Feed, Wt. Ratio	0.3	0.3	1.00
<u>Yields, Wt. % MAF Feed</u>			
CH ₄	1.1	1.1	1.2
C ₂ H ₆	1.2	1.2	1.5
C ₃ H ₈	1.6	1.6	4.6
iC ₄ H ₁₀	0.2	0.1	5.0
nC ₄ H ₁₀	1.0	1.2	0.8
C ₅ x 150°C Dist.	7.0	9.1	52.5
150 x 200°C Dist.	1.7	8.4	10.4
200 x 400°C Dist.	16.9	16.1	6.3
MEK-Sol. + 400°C Residue	67.5	60.2	19.0
MEK-Insol. + 400°C Residue	2.9	2.4	3.4
Conversion, Wt. % Feed	29.6	37.4	77.6
H ₂ Consumed, Wt. % Feed	2.64	3.14	6.85
(C ₁ -C ₃) x 100/Conversion	13.4	10.5	9.5

TABLE V

Hydrocracking of Benzene with Zinc Chloride Catalyst

Temperature = 427°C - Residence Time at Temperature = 60 min.

Total Hot Pressure = 4200 psig

Yields, Wt. % of Benzene Feed

CH ₄	-	.04
C ₂ H ₆	-	.09
C ₃ H ₈	-	.92
iC ₄ H ₁₀	-	.43
nC ₄ H ₁₀	-	.14
C ₅ H ₁₂	-	.24
Other C ₆ 's	-	.42
Benzene	-	<u>99.00</u>
Total		101.28

H₂ Consumed = 0.94 wt. %

TABLE IV

Comparison of Molten Salt Catalysts for Pyrene Hydrocracking

All Runs - 60 min. Residence Time at Temperature

Run No.	11	12	13	14	15	16	17	18	
Temperature, °C	427	↔							300
Total Hot Pressure, psig	4200	↔							3000
Catalyst	ZnCl ₂	↔							SnCl ₂ AIBr ₃
Catalyst/Pyrene, Wt. Ratio	0.07	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Catalyst Additive	None	None	SnCl ₂	MoO ₃	HCl	H ₂ O	None	None	
Additive/Pyrene, Wt. Ratio	--	--	.02	.05	.021	0.08	--	--	
Yields, Wt. % Pyrene									
CH ₄	0.0	0.8	0.8	1.0	2.3	1.0	0.0	1.8	
C ₂ H ₆	0.1	1.4	1.6	2.3	4.3	2.3	0.2	1.8	
C ₃ H ₈	0.5	11.2	11.4	9.7	11.1	10.6	0.2	25.2	
iC ₄ H ₁₀	0.6	9.6	9.8	8.1	8.5	8.2	0.0	24.1	
nC ₄ H ₁₀	0.1	1.7	1.6	1.2	1.8	1.1	0.0	19.1	
C ₅ x 150°C Dist.	6.3	52.7	52.4	53.2	45.3	{ 0.0		24.5	
150 x 200°C Dist.	0.3	1.7	1.8	2.1	1.3	{ 66.8		--	
200 x 280°C Dist.	2.0	1.9	2.7	6.2	1.6	{ 0.9		--	
280 x 340°C Dist.	1.0	3.3	3.3	4.7	0.9	{ 3.0		--	
340 x 390°C Dist.	36.8	11.5	12.2	7.2	0.6	{ 11.8		--	
Pyrene	53.1	6.5	4.8	2.4	0.4	{ 49.9		--	
+Pyrene	--	2.5	2.7	3.1	9.1	{ 3.6		0.0	
Coke	--	5.0	4.2	8.6	21.5	{ 4.8		0.0	
Total	101.2	109.2	109.3	109.8	108.7	110.2	101.8	112.4	
H ₂ Consumed, Wt. % Pyrene	1.23	9.21	9.31	9.85	8.68	10.23	1.8	12.4	

Figure 1
FLOW DIAGRAM
FOR AUTOCLAVE UNIT

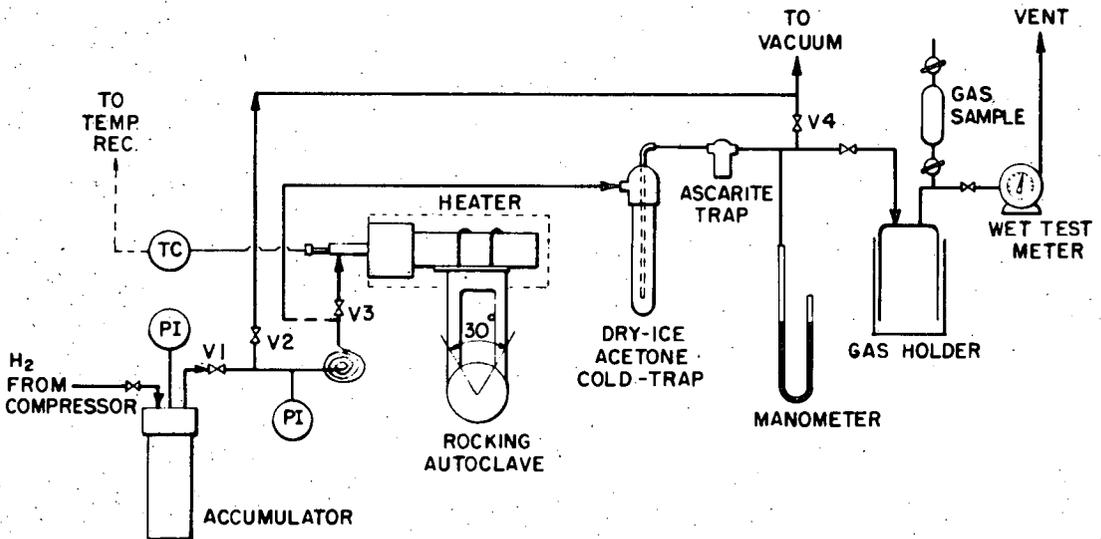


FIGURE NO. 2

Ammonia Adsorption Isotherms

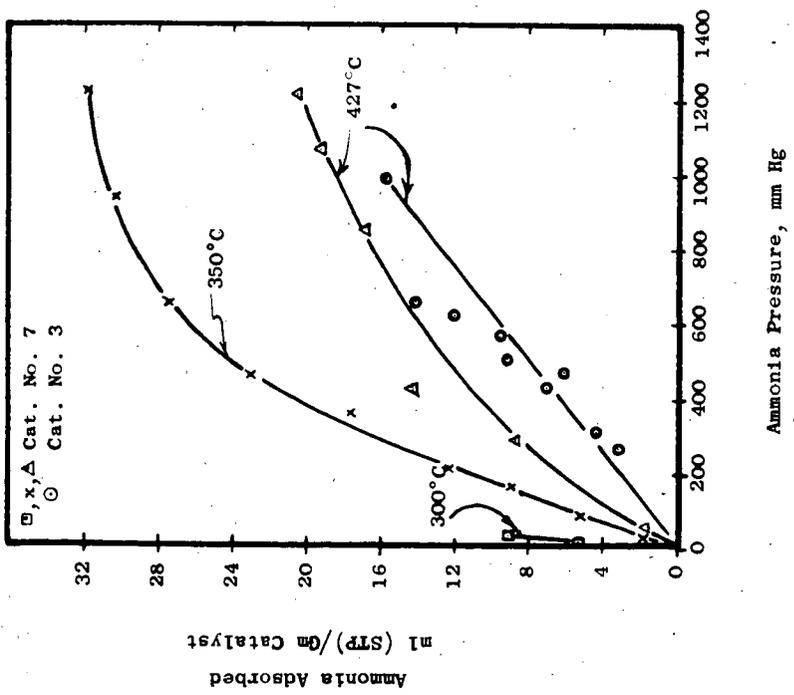


FIGURE NO. 3

The Effect of Ammonia Partial Pressure on Distillate Yields

