DEL/RC/91051-74

ADVANCED LIQUEFACTION USING COAL SWELLING
AND CATALYST DISPERSION TECHNIQUES

Report Number Q-04
Quarterly Technical Progress Report
for
July-September 1992

Project Manager: D. C. Cronauer

Principal Investigators: C. W. Curtis,
Auburn University
C. Gutterman,
FWDC
S. Chander,
Pennsylvania State Univ.

Work Performed Under Contract No. DE-AC22-91PC91051

For

U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By

Amoco Oil Company
Research and Development Department
Post Office Box 3011
Naperville, IL 60566

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fr

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TECHNICAL STATUS

This technical report is being transmitted in advance of DOE review, and no further dissemination or publication will be made of the report without prior approval of the DOE Project/Program Manager.

NOTICE

This report was prepared by the organization named below as an account of work sponsored by the United States Department of Energy (DOE). Neither DOE, members of DOE, the organization named below, nor any person acting on behalf of any of them: (a) makes any warranty, expressed or implied, with respect to the use of any information, apparatus, method, or process disclosed in this report or that such use may not infringe privately owned rights; or (b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Prepared by
Amoco Oil Company (Amoco Corporation)
Naperville, Illinois

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	6
SUMMARY OF RESULTS AND ACTIVITY	8
PROJECT DOCUMENTATION	9
TASK 1.0: LABORATORY-SCALE EXPERIMENTATION	9
Subtask 1.1: Laboratory Support	9
TASK 2.0: LABORATORY-SCALE OPERATION	9
Subtask 2.1: Coal Pretreatment	9
Subtask 2.2: Catalyst and Swelling Studies	9
Subtask 2.3: Reactivity of Swelled Coals with Dispersed Catalysts	18
Subtask 2.4: Bench-Scale Studies	22
Subtask 2.5: Solids Separation/Alternative Bottoms Processing	22
CONCLUSIONS AND FUTURE WORK	23
ACKNOWLEDGMENTS	24
TABLES	25
FIGURES	45
APPENDIX A	54

EXECUTIVE SUMMARY

The overall objective of this project is to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. The approach integrates all aspects of the coal liquefaction process including coal selection, pretreatment, coal swelling with catalyst impregnation, liquefaction, product recovery with characterization, alternate bottoms processing, and carrying out a technical assessment including an economic evaluation. The project is being carried out under contract to the United States Department of Energy. The primary contractor is Amoco Oil Company, and the subcontractors are Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

Experimentation is under way at all of the above facilities. The solvent and coal feedstocks have been obtained, and the beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal has been carried out. Sulfurous acid-treated Black Thunder coal containing about 4 wt% ash has been prepared for initial experiments. Further coal beneficiation was not achieved using gravity separation. Coal swelling ratios were determined with a wide variety of solvents using finely pulverized samples of Black Thunder subbituminous, Illinois No. 6 bituminous, and Martin Lake lignite. Only marginal levels of coal swelling were observed for the hydrocarbon solvents, but swelling greatly increased with the use of solvents having heteroatom functionality. The swelling ratios of solvent blends were much greater than those derived from a linear correlation between the pure solvents.

The activity of various catalyst precursors for pyrene hydrogenation and coal conversion was measured. Molyvan-L yielded higher conversion of pyrene to hydrogenated products than did the other catalyst precursors. Higher coal conversions were observed for the SO₂-treated coal than the raw coal, regardless of catalyst type. Coal conversions were highest for Molyvan-L, molybdenum naphthenate, and nickel octoate, respectively. Sulfur addition greatly promoted the following precursors: molybdenum naphthenate, nickel naphthenate, and iron naphthenate. Pyrene conversion was greatest for the nickel octoate and Molyvan-L precursors. Low activity was shown by molybdenum naphthenate, iron naphthenate, chromium (III) 2-ethylhexanoate, and vanadium naphthenate.

The literature concerning coal swelling, both alone and in combination with coal liquefaction, and the use of dispersed or unsupported catalysts in coal liquefaction has been updated.

Bottoms processing consists of a combination of the ASCOT process coupling solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting solids within the coke drum. Initial results indicate that a blend of butane and pentane used near the critical temperature of butane is the best solvent blend for producing a yield/temperature relationship of proper sensitivity and yet retaining an asphalt phase of reasonable viscosity.

PROGRAM OBJECTIVES

The objective of this project is to develop a new approach to the direct liquefaction of coal to generate an all-distillate product slate at a sizable cost reduction over current technology. The approach will integrate all aspects of the coal liquefaction process, including coal selection, pretreatment, coal swelling with catalyst impregnation (and parallel runs with dispersed catalyst); coal liquefaction experimentation including solvent evaluation, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The three tasks of this program are:

1. Task 1: Laboratory-Scale Experimentation--The goals are to obtain samples of coals and Wilsonville-derived solvents and vacuum tower bottoms and to establish experimental procedures.
2. Task 2: Laboratory-Scale Operation--The goals are to:
 - (1) Reduce the concentration of mineral matter and alkali metals in low rank coals, (2) swell and impregnate coals with dispersed catalysts, (3) characterize the resulting catalyst solids, (4) evaluate the effectiveness of the procedures using liquefaction runs, and (5) study solids separation and alternative bottoms handling, which includes observing pumping characteristics, deasphalting, and coking.
3. Task 3: Technical Assessment--The goals are to analyze the data, develop descriptive models, and carry out an economic evaluation.

The research is being carried out in cooperation with the following subcontractors: Foster Wheeler Development Corporation (FWDC), Auburn University (AU), Pennsylvania State University (PSU), and Hazen Research Inc. Appropriate meetings and correspondence are being maintained to ensure effective completion of the project.

PROGRAM MILESTONES

The keystones are based upon the date of approval to initiate experimentation, namely obtaining the authorization of the NEPA form. This authorization was obtained on May 28, 1992. The first key milestone was to obtain the appropriate feed stocks for the experiments. The second milestone was preparing the beneficiated bulk samples of coal for subsequent experiments. The feedstocks have been obtained, and the beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal has been done by Hazen Research Inc. The laboratory-scale coal swelling and catalyst screening program has started. Sufficient data must be obtained from the latter program to establish conditions for bench-scale liquefaction experiments to start during the fourth quarter. The batch deasphalting and coking experiments will be completed by the end of the fifth quarter after the start of experimentation by FWDC. Experimentation should be essentially complete by the end of the seventh quarter in order to complete the project within a two-year period that started on May 28, 1992.

SUMMARY OF RESULTS AND ACTIVITY

The objective of this project is to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. All aspects of the process are included with emphasis upon coal pretreatment, coal swelling with catalyst impregnation, and alternate bottoms processing. Research is under way at Amoco Oil Company, Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

Beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal has been carried out including the preparation of sulfurous acid-treated Black Thunder coal containing about 4 wt% ash. The experimental study of coal swelling is nearly complete. Coal swelling ratios have been determined with a wide variety of solvents. Only marginal levels of coal swelling were observed for the hydrocarbon solvents, but high levels were found with solvents having heteroatom functionality. Blends were superior to pure solvents. The activity of various catalyst precursors for pyrene hydrogenation and coal conversion was measured. Higher coal conversions were observed for the SO₂-treated coal than the raw coal, regardless of catalyst type. Coal conversions were highest for Molyvan-L, molybdenum naphthenate, and nickel octoate, respectively. Bottoms processing consists of a combination of the ASCOT process coupling solvent deasphalting with delayed coking. Initial results indicate that a blend of butane and pentane used near the critical temperature of butane is the best solvent blend for producing a yield/temperature relationship of proper sensitivity and yet retaining an asphalt phase of reasonable viscosity.

The literature concerning coal swelling, both alone and in combination with coal liquefaction, and the use of dispersed or unsupported catalysts in coal liquefaction has been updated.

Near-term activity is centering upon (1) further beneficiating Black Thunder coal using froth flotation, (2) undertaking swelling experiments in combination with catalyst impregnation using raw and SO₂-treated Black Thunder coal, (3) studying the liquefaction of swollen coals that have been impregnated with catalyst precursors, and (4) further defining the best solvent for bottoms processing.

PROJECT DOCUMENTATION

The Project Management Plan, Milestone Schedule/Manpower Plan, and Cost Plan are being revised to reflect the late approval (NEPA) that started experimentation on May 28, 1992. The revision will be issued after this quarterly report.

Task 1.0: Laboratory-Scale Experimentation

Subtask 1.1: Laboratory Support

The feedstocks are on hand, and analyses are complete as reported below and in the previous quarterly.

Task 2.0: Laboratory-Scale Operation

Subtask 2.1: Coal Pretreatment

Bulk samples of both Martin Lake lignite and Black Thunder subbituminous coal were pretreated to recover beneficiated coal for subsequent swelling, catalyst impregnation, and liquefaction experiments. The treatment included crushing, sizing, contacting the coarse fraction with aqueous SO_2 to remove alkali and alkaline metals, and subsequent gravity separation to recover a fraction having particularly low ash content. Two 55-gallon drums of Martin Lake (Texas) lignite and 3 of Black Thunder subbituminous coal were processed at Hazen Research Inc. The SO_2 -treated subbituminous and lignitic coals were subjected to heavy media (finely dispersed magnetite) cyclone tests. As reported in the previous quarterly, it was not possible to isolate an overhead (float) fraction having a coal recovery of about 80 wt%. Therefore, the bulk samples of raw and SO_2 -treated coals were returned to Amoco for characterization and use. Additional exploratory runs will be done at Hazen Research using the SO_2 -treated coals.

About one 55-gallon drum of SO_2 -treated Black Thunder has been partially dried using a stream of nitrogen at ambient temperature. This coal has been characterized, a portion pulverized, and it is being used in swelling experiments.

Subtask 2.2: Catalyst and Swelling Studies

Coal Swelling Background:

The literature concerning coal swelling, both alone and in combination with coal liquefaction, has been updated using Amoco's library computer search facilities. The results of the search were reported in the previous quarterly. The following is a summary of the conclusions of that search.

The proposal of van Krevelen that coals are three-dimensionally cross-linked macromolecular networks is generally being accepted. When brought into contact with most organic solvents, coals absorb the solvent and swell. The amount of swelling depends on both the coal and the solvent. The two factors which control the amount of swelling are the magnitude of

the solvent-coal interactions and the cross-link density of the coal. Expressions have been derived to describe these terms. Another aspect is that coals can behave as either a glass or rubber with a transition zone. In a glassy state, the macromolecular chains are constrained and diffusion through the coal matrix is quite slow. For reference, as-mined coals exhibit glass-like properties. In the rubbery state, the macromolecular chains can move relatively freely, and diffusion rates in the solid approach those in liquids. Some solvents can cause a glass-to-rubber transition to occur in coals.

Coal swelling solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents are significantly less than those in hydrogen bonding solvents. The most effective solvents are those containing a nitrogen or oxygen atom possessing an unshared pair of electrons.

The swelling data are consistent with a covalent cross-linked structure of coal. This is supported by the high swelling observed in hydrogen bonding solvents. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with new coal-solvent hydrogen bonds. If the coal-coal hydrogen bonds are active cross-links, the replacement would result in a lower cross-link density which would cause swelling to increase. The weak hydrogen bonding solvents result in less swelling since more coal-coal hydrogen bonds remain intact. The decrease in swelling in high carbon content coals could be attributed to possible physical stacking interactions between polynuclear aromatics (PNA's) in the coal structure, although there is no supporting evidence in the literature. These interactions will not be easily altered by materials which are liquids.

The best correlation between the extent of swelling and coal rank is that derived from experimentation with pyridine. A relatively constant swelling ratio was observed in pyridine for coal samples with carbon contents of 65% to 85%. A dramatic decrease in the swelling ratio was observed above 86% C.

It appears that swelling coal in suitable solvents prior to liquefaction could improve conversion and product quality. This has been demonstrated, and the application of this technique in combination with catalyst impregnation in coal liquefaction should decrease the costs of commercial liquefaction.

Coal Swelling Experimental Procedure:

The initial swelling experiments were made using the following three coal samples that were prepared in a previous DOE project: (1) Martin Lake lignite, (2) Black Thunder subbituminous, and (3) Illinois No. 6 bituminous coals. The coals were handled in nitrogen whenever possible. These samples were sieved and ground to -325 mesh under nitrogen and dried overnight in a vacuum oven. Following these runs, experiments were carried out using coarse (8 x 60 mesh) samples of raw and SO₂-treated Black Thunder coal that had only been partially dried to about 8 wt% moisture content at ambient temperature in nitrogen.

The experimental swelling procedure for the first set of samples consisted of placing samples of dry coal in a 1 mm. o.d. tube followed by centrifuging for 60 minutes. The height of the coal was measured as h_1 . After breaking up the column of packed coal, solvent in excess was introduced and the tube was vigorously shaken to ensure thorough mixing. The slurry was centrifuged after specified times and the height was measured as h_2 . The swelling ratio was defined as the ratio of the resulting heights of swelled and raw coal ($Q = h_2/h_1$). In the experiments with the coarse coal samples, 10 ml conical centrifuge tubes were used.

Coal Swelling Results:

1. Reproducibility:

During the series of swelling experiments, runs were made to determine reproducibility; in addition, two laboratory technicians ran parallel tests. The results are given in Tables I and II. In summary, reproducibility was good. At low swelling ratios, such as those of the methanol runs (average Q of 1.28), the standard deviation averaged about ± 0.06 . At high swelling ratios (tetrabutyl ammonium hydroxide, Q averaging about 2.5), the standard deviation averaged about ± 0.14 .

2. Effect of Solvent Type and the Interaction with Coal Pretreatment:

The swelling ratios were determined with a wide variety of solvents using the finely pulverized (through 325 mesh) samples of Black Thunder subbituminous, Illinois No. 6 bituminous, and Martin Lake lignite. The results are given in Table III. Subsequent experiments were carried out using 8X60 mesh size fractions of raw and SO_2 -treated Black Thunder coal; see Table IV.

Only marginal levels of coal swelling were observed for the hydrocarbon solvents. This included hexane, cyclohexane, single-ring aromatics, and tetralin, which is a hydroaromatic hydrogen-donor solvent often used in coal liquefaction experiments.

As shown in Table III, swelling greatly increased with the introduction of hetero-functionality. Equilibrium (96 hour contact) swelling ratios of the three coals with alcohols and ketones fell in the range of 1.15 to 1.4. There appeared to be no consistent effect of the type (molecular weight) of alcohol or ketone, but the Black Thunder coal swelled to a greater extent than the other coals. Cresol was a more effective swelling agent than the above oxygenates in the case of Illinois No. 6 coal, but it was the same for the other coals. The results with methyl acetate were the same as those of the above oxygenates. Tetrahydrofuran (THF) was a significantly more effective coal swelling solvent than the other oxygenates. The Q ratios ranged from 1.38 to 1.63.

The nitrogen-containing compounds varied greatly in their effectiveness to swell these coals. The highly polar compound, tetrabutylammonium hydroxide (TBAH), was very effective with a range of Q ratios of 2.18 to 2.66. Aniline was quite effective for Illinois No. 6 and Black Thunder coals (1.94 and 1.64, respectively), but it was essentially ineffective

(1.19) for Martin Lake lignite. Nitrobenzene was poor for all three coals (1.11 to 1.19).

Dimethylsulfoxide was tested due to its unusual solvent properties in other systems. It was found to be particularly effective for the Black Thunder and Illinois No. 6 coals and moderately effective for Martin Lake lignite (2.39, 2.15, and 1.63, respectively).

The results of coal swelling experiments carried out with 8X60 mesh size fractions of both raw and SO₂-treated Black Thunder coal are given in Table IV. There appeared to be little or no effect of coal particle size upon the swelling ratio. However, the SO₂-treated coal swelling was significantly greater than that of the raw coal. As anticipated, the removal of alkali and alkaline earth ions from the subbituminous coal reduced the interaction of coal species with each other (particularly in the case of divalent metal ions).

In summary, the above differences in swelling are attributed to the interaction of the solvent with the various bonds present in coal. The low rank coals contain significant amounts of ionic and hydrogen bonds due to the presence of a relatively large number of polar functional groups, while the high rank coals contain more charge transfer complexes because of their higher aromatic content. TBAH, which is a very basic solvent, interacts with the ionic and hydrogen bonds readily, thus swelling the Martin Lake lignite to the greatest extent. This is followed by Black Thunder coal and Illinois No. 6. On the other hand, THF disrupts charge transfer complexes, which are predominant in Illinois No. 6, a higher rank coal, thus resulting in a swelling trend opposite to that of TBAH. The increase of swelling ratio in the case of SO₂ treatment is an obvious extension of this theory, especially with the removal of divalent metal ions, such as calcium.

As shown in Figure 1, an attempt was made to correlate coal swelling with solvent dipole moment (polarity). While coal swelling generally increased with increasing solvent dipole moment, the correlation was poor.

3. Effect of Solvent Blends:

The results of the initial coal swelling experiments made with 325 mesh coal samples and blends of tetralin (TET) and isopropanol (IPA) are shown in Table III and Figure 2. There was a high level of synergism with an advantage of using these blends over the pure solvents. In all cases, the swelling ratios were much greater than those derived from a linear correlation between the pure solvents. The greatest effects were observed for the experiments made with Black Thunder and Illinois No. 6 coals.

As shown in Figures 3 through 5, the synergism of coal swelling solvents also was demonstrated for the following systems: tetrahydrofuran/water, methanol/water, dimethyl sulfoxide/tetralin, methanol/tetralin, and isopropanol/water.

Experimentation was also carried out with the 8X60 mesh fractions of raw and SO₂-treated Black Thunder coal, as given in Table IV. Again, there were high levels of synergism of solvent blends with both samples of coal.

In summary, there is a distinct advantage of using solvent blends to swell coal. This is of particular importance, because relatively low levels of swelling agent would be needed to be effective in treating coal feed slurries for the liquefaction plant. This aspect should be tested. However, it will be difficult, because the recycle solvents are very dark, and determining swelling ratios may not be possible. Of course, the ultimate evaluation entails swelling coal, impregnating it with a dispersed catalyst, and achieving increased coal conversion in the liquefaction unit.

4. Rate of Coal Swelling:

As shown in Figure 6, finely pulverized (through 325 mesh) Black Thunder coal quickly reaches its equilibrium level of swelling within about 4 hours. It is anticipated that coarser fractions will take longer times. Such experimentation is planned as part of the catalyst impregnation studies.

Literature and Patent Literature Review of the Use of Dispersed Catalysts in Coal Liquefaction:

This review covers a literature and patent survey on the use of dispersed or unsupported catalysts in coal liquefaction. It updates previous reviews, such as those of Derbyshire (1988),¹ Charcosset and Genard (1987),² and Narain et al. (1987),³ with recent developments in process and fundamental studies, particularly in catalyst dispersion methods and characterization of catalyst activity. It was conducted to provide leads on effective dispersion techniques and catalytic components and to identify an effective dispersed catalyst process for subbituminous coal and lignite. The complete review, including the above cited references, is included in the Appendix, and the Summary and the Conclusions and Recommendations are given below.

1. Summary:

Sulfides of Mo, Co, W, and Fe have been identified as active catalysts since the pre-World War II development of coal liquefaction, and investigations, particularly of Fe and Mo catalysts, continue. In spite of recent progress in analytical techniques that have allowed better characterization, much remains to be understood of the basis and origin of catalyst activity. The degree of dispersion and catalyst active form largely affect catalyst activity; these factors are, in turn, determined by the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given set of liquefaction conditions.

The catalyst active form has generally been deduced from characterization of the catalyst after liquefaction. In general, when sufficient sulfur is present (either as added sulfur compounds or as coal sulfur), the catalyst is largely present in the sulfide form. When insufficient or no sulfur is present, the catalyst is largely present as a reduced form (such as the metal or carbide) of the precursor. The general consensus appears to be that the non-stoichiometric sulfide pyrrhotite (Fe_{1-x}S) is the active form for Fe; recent studies suggest that a similar non-stoichiometric sulfide

may be the active form for Mo. In addition to acting as sulfiding agents for the formation of the active sulfide form of the catalyst precursor, added sulfur compounds can enhance liquefaction performance by any of all of the following: (1) they may act as free radical initiators, (2) they may alleviate catalyst poisoning (e.g., by nitrogen), and (3) they help maintain the catalyst in the active form by preventing reoxidation of the catalyst, particularly with high-moisture coals.

The degree of catalyst dispersion has generally been inferred from liquefaction performance. Catalyst powders enhance coal conversion over thermal liquefaction, provided the catalyst is activated and is finely dispersed. Soluble precursors give better liquefaction performance (in terms of coal conversion and oil yield) than thermal liquefaction, and their effectiveness depends on the quality of the donor solvent (if there is any), the coal type, and the catalyst activation conditions. With an effective catalyst, donor solvent may not be necessary. The dependence on coal type relates to surface properties that affect wettability and dispersability. For example, iron precursors may be better dispersed on low rank coals which contain surface functional groups with which the iron may interact. In general, catalyst powders are less effective than soluble or impregnated precursors. An exception may be very fine (nanometer-sized) catalysts generated from microemulsion-based techniques or aerosol precursors produced from laser pyrolysis or flame processes.

Recent research efforts have focused on catalysis by Fe and Mo. Oil-soluble Molybdenum additives, organometallic precursors (such as naphthenates, carbonyls, and molybdic acid), and various molybdates have been demonstrated as effective Mo catalyst precursors, for low and high rank coals. Compared with Fe, Mo has better hydrogenation activity; however, the higher cost of Mo has motivated development of low-Mo catalysts, such as disposable Fe catalysts promoted by low amounts of Mo. The low activity of Fe catalysts can also be improved by increasing surface area and by sulfation; the latter can also inhibit sintering or agglomeration, thus leading to better catalyst activity maintenance. These enhancements may make Fe catalysts attractive for liquefaction of low rank coals onto which they may be more easily and better dispersed, compared with higher rank coals.

Recommended areas for further research on the development of improved catalysts include (1) dispersion methods combining coal pretreatment with soluble catalysts, such as simultaneous coal swelling and catalyst introduction, (2) Molybdenum additives as dispersed catalysts, particularly determination of catalyst active form, activation conditions, and catalyst mechanism, including the role (if any) of the phosphorus in the additive, (3) multicomponent catalysts, particularly on fundamentals of catalysis mechanism and metal interaction(s) and on combinations other than Fe + Mo, (4) treatment of dispersed catalysts, such as sulfation, to produce catalysts with higher activity and better activity maintenance, and (5) methods of catalyst recovery.

2. Conclusions and Recommendations:

(Reference is made to the Appendix for cited references)

a. On factors affecting dispersed catalyst activity:

- The degree of dispersion and catalyst active form largely affects catalyst activity. These factors are in turn determined by the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given set of liquefaction conditions. For example, at temperatures $> 275^{\circ}\text{C}$, Mo-based catalysts from soluble precursors³⁴ and from FeOOH^{34a} appear to be activated, whereas activation of MoS_2 fine powder occurs at temperatures above 325°C .
 - The active form of the catalyst has generally been deduced from characterization of the catalyst after liquefaction. This assumes that the catalyst form remains unchanged between liquefaction and the characterization. In general, when sufficient sulfur is present (either as added sulfur compounds or as coal sulfur), the catalyst is largely present in the sulfide form. When insufficient or no sulfur is present, the catalyst is largely present as a reduced form of the precursor (e.g., metal, carbide).
 - The addition of sulfur compounds during liquefaction has generally resulted in enhanced liquefaction performance. This has been attributed to various reasons: (1) they act as sulfiding agents for the formation of the active sulfide form of the catalyst precursor, (2) they may act as free radical initiators, (3) they may alleviate nitrogen poisoning of the catalyst, and (4) they help maintain the catalyst in the active form by preventing reoxidation of the catalyst (particularly with high-moisture coals).
 - Better dispersed catalyst activity maintenance has been achieved in the following research areas:
 - (1) sulfation, which can inhibit sintering or agglomeration of dispersed catalysts, which are generally less stable than supported catalysts with respect to sintering, (2) use of oil-soluble Molyvan additives which can reduce coke formation, and (3) use of phosphorus promotion with Mo-based catalysts. In the latter area, in addition to possibly preventing agglomeration of the catalyst particles, P promotion can change the acidic properties of the support (increase or decrease, depending on the P loading and the structure of the surface phosphates).
- b. On the relative performance of dispersed catalysts:
- Catalyst powders enhance coal conversion over thermal liquefaction if the catalyst is fine enough to achieve good dispersion and if the catalyst is activated at the liquefaction conditions used.

- Soluble precursors give better liquefaction performance (in terms of coal conversion and oil yield) than thermal liquefaction.
 - The effectiveness of soluble precursors depends on the quality of the donor solvent (if there is any), the coal type, and the catalyst activation conditions. In general, donor solvent may be unnecessary with an effective catalyst. The dependence on coal type relates to surface properties that affect wettability and dispersability. For example, water-soluble precursors may be more effective with high-moisture coal. Iron precursors may be more dispersed on low rank coals which contain surface functional groups with which the iron may interact.
 - In general, catalyst powders are less effective than soluble or impregnated precursors. An exception may be very fine (nanoscale) catalysts generated from microemulsion-based techniques or aerosol precursors produced with flame processes.
- c. On catalysis by Mo and Fe:
- Mo-based catalysts have been regarded as providing a source of H atoms which induce cleavage and stabilize radicals.
 - Oil-soluble additives (such as Molyvan additives), organometallic precursors (such as naphthenates and carbonyls of Mo), and various molybdates have been demonstrated as effective Mo catalyst precursors, for low and high rank coals.
 - The mechanism for Fe catalysis appears to depend on residence time. At short residence time, Fe catalysts reduce coal conversion due to the slowing of coal radical propagation. However, at longer residence times, Fe catalysts can accelerate both direct hydrogenation and reactions involving H-transfer from the donor solvent.
 - The low activity of Fe catalysts can be improved by increasing surface area, sulfation, and/or promotion with low concentrations of other metals (such as Mo). These enhancements may make Fe catalysts attractive for liquefaction of low rank coal whose higher concentration (compared with high rank coals) of surface functional groups may provide greater interaction with the Fe, thereby leading to more facile and greater dispersion.
 - Compared with Fe, Mo has better hydrogenation activity; however, the higher cost of Mo has motivated development of low-Mo catalysts, such as Fe-based disposable catalysts promoted by low amounts of Mo.

d. Recommended areas of research for the development of improved catalysts:

- Combination of coal pretreatment with soluble precursor for catalyst dispersion: In particular, the impregnation of the catalyst precursor onto the coal with swelling solvents appears promising, based on the limited information in the open literature and preliminary results obtained to date in this DOE contract. The use of blends of swelling solvents to simultaneously swell the coal and introduce the catalyst precursor into the (swollen) coal may prove to be effective. Investigations with both oil- and water-soluble precursors in compatible swelling solvents are recommended with coals of varying moisture contents.
- Oil-soluble Molyvan additives as dispersed catalysts: Process conditions for liquefaction with these additives, which have been demonstrated to be effective for both bituminous (Illinois No. 6) and subbituminous (Black Thunder) coals, need to be optimized. Other recommended areas of research are catalyst active form, activation conditions, and catalysis mechanism, including the role (if any) of the phosphorus in the additive.
- Multicomponent catalysts, particularly on fundamentals of catalysis mechanism and metal interaction(s): Since Derbyshire's 1988 review,² where further work with multicomponent catalysts was recommended, numerous investigations have been conducted, primarily with Fe + Mo catalysts. Promotional or synergistic benefits (with respect to coal conversion, oil yield, or sulfur removal, for example) have been reported with Fe + Mo. The combination of hydrocracking and hydrogenation functionalities in one catalyst using combinations other than Fe + Mo can provide opportunities to tailor other catalysts with enhanced liquefaction performance. Although numerous other metal combinations have been claimed in the patent literature, very little is known about the catalyst mechanism or the metal interaction(s).
- Treatment (such as sulfation) of multicomponent catalysts to produce catalysts with higher activity and better activity maintenance: Although one attraction of a dispersed catalyst is that it can be disposable, one with good activity maintenance can be recycled. This can potentially reduce catalyst recovery and/or disposal requirements. Further research on the combination of high-activity multicomponent catalysts with sulfation, such as the sulfated Fe-Mo oxides catalyst systems developed at the University of Pittsburgh, is recommended. One possible area of research is the use of Molyvan additives, whose phosphorus promoters may

enhance stability with respect to sintering, in these catalysts.

- Methods of catalyst recovery: There are numerous patent claims and investigations on catalyst recovery, particularly of Mo; all of the recovery methods are based on solvent extraction. However, there has been limited investigations on optimization.

Subtask 2.3: Reactivity of Swelled Coals with Dispersed Catalysts

Preliminary Experimentation

A series of experiments was performed to evaluate the activity of two catalysts, Molyvan L and molybdenum naphthenate, for pyrene hydrogenation in the presence and absence of added Illinois No. 6 coal. These experiments laid the groundwork for the development of the catalyst reactivity screening test that is described in the next section.

Illinois No. 6 coal was reacted individually and combinatorially with pyrene to determine its effect on the reactivity of pyrene in the presence and absence of catalysts. The amount of coal conversion achieved was determined in some of the experiments. The catalysts used were molybdenum naphthenate and Molyvan-L without the addition of excess sulfur. The reaction conditions for this study are given in Table V. The pyrene was mixed directly with the coal or resid and reacted at 426°C for 30 min with 1250 psig H₂ introduced at ambient temperature. The product distribution of pyrene with coal in the presence of Mo naphthenate is given in Table VI. Likewise, the product distribution from these same systems with Molyvan-L is presented in Table VII.

At equivalent reaction conditions, Molyvan-L yielded higher conversion of pyrene to hydrogenated products than did molybdenum naphthenate. The primary hydrogenated product in both cases was dihydropyrene (DHP), with trace amounts of hexahydropyrene (HHP) being formed.

The effect of added components on pyrene hydrogenation to partially saturated species was substantial. Without any added component and with Mo naphthenate as catalyst, pyrene conversion averaged ~9.1%, producing dihydropyrene (DHP) as the product. By contrast, with coal added to the system, the amount of pyrene conversion increased, yielding DHP as the primary product with a small amount of tetrahydropyrene (THP) and a trace amount of hexahydropyrene (HHP) being formed. As the weight percent of coal increased in the pyrene system, the amount of pyrene conversion substantially increased from ~23% pyrene conversion with 6.4% coal to ~38% with 19.2% coal.

A similar set of reactions was performed with pyrene and Molyvan-L (Table VI). Similar results were obtained with Molyvan-L as with Mo naphthenate. The pyrene conversion was least when no coal was present, but increased when it was present. With coal addition, the amount of pyrene conversion increased as the weight percent of coal increased, ranging from 21.4% for 6.4% coal loading to 38.0% for 19.2% coal loading. As with Mo naphthenate, the coal plus the resid increased pyrene conversion.

Coal conversions in selected systems using Mo naphthenate and Molyvan-L are presented in Table VIII. The amount of coal present may have made a difference in the conversion in both systems. The error for these experiments is quite high, making conclusions regarding coal conversion difficult. The procedure for determining coal conversion was revised in order to obtain more consistent results in the catalyst screening test given in the next section.

Developing the Catalyst Screening Test

A method was developed to determine the catalytic activity of a number of different catalysts for pyrene hydrogenation and coal conversion. The catalyst precursors tested were (1) molybdenum naphthenate, (2) Molyvan-L, (3) iron naphthenate, (4) nickel naphthenate, (5) nickel octoate, (6) chromium (III) 2-ethylhexanoate, and (7) vanadium naphthenate. Their activity was measured in terms of pyrene hydrogenation to partially saturated products and coal conversion to THF soluble materials.

The experimental system consisted of reacting the following in a shaken micro-autoclave reactor: 1.5 g of pyrene, 20 wt% coal, and a nominal 600-700 ppm of active metal from the catalyst precursor based on feed. The coals used were untreated Black Thunder coal and SO₂-treated Black Thunder coal. Proximate and ultimate analyses for both of these coals are given in Table IX. The reactions were performed at 410°C for 30 minutes and were agitated at 450 cpm. Sulfur was not added to the system. The analysis of the system included pyrene conversion and pyrene hydrogenation products as determined from gas chromatographic analysis, as well as conversion of coal to THF solubles.

The pyrene conversion and coal conversion results for Black Thunder and SO₂-treated Black Thunder coals are presented in Tables X and XI, respectively. The product distributions for the hydrogenation products of pyrene are presented in Tables XII and XIII for the reactions with Black Thunder and SO₂ treated Black Thunder coals, respectively.

The untreated Black Thunder coal responded most favorably to the catalyst precursors, Molyvan-L and nickel octoate. These two catalysts both resulted in an average coal conversion of 73%. However, higher coal conversions were observed on the average for the SO₂-treated coals, regardless of catalyst type. Average coal conversions for SO₂-treated Black Thunder coal of 90.3%, 85.7%, and 84.4% were obtained for Molyvan-L, molybdenum naphthenate, and nickel octoate, respectively.

The catalyst precursors that had the least effect on coal conversion for untreated Black Thunder coal were molybdenum naphthenate and chromium (III) 2-ethylhexanoate at average coal conversions of 48.2% and 49.2%, respectively. For the SO₂-treated Black Thunder coal, chromium (III) 2-ethylhexanoate resulted in the least conversion of 54.8%. Several catalysts yielded substantially increased coal conversion in the presence of the additional sulfur in the SO₂ treated Black Thunder. The coal conversion with molybdenum naphthenate increased from an average coal conversion of 48.2% for the untreated coal to 85.7% for the SO₂ treated coal. Likewise, with nickel naphthenate the coal conversion increased from an average of 62.7% for the untreated coal to 73.9% for the SO₂ treated coal. Iron naphthenate increased in its activity as well by

increasing coal conversion from an average of 54.2% for the untreated coal to 63.4% for the SO₂ treated coal.

Pyrene conversion varied considerably depending upon the type of catalyst present and the amount of sulfur in the system (Tables X and XI). The pyrene conversion in the untreated Black Thunder system was greatest for the systems of nickel octoate and Molyvan-L. The catalysts that showed low activity were molybdenum naphthenate, iron naphthenate, chromium (III) 2-ethylhexanoate, and vanadium naphthenate. Nickel naphthenate resulted in intermediate but variable activity for pyrene hydrogenation. The presence of sulfur in the SO₂-treated coal system changed the activity of some of the catalysts for pyrene hydrogenation. Molybdenum naphthenate increased substantially from 3.4% in the untreated system to 26.2% in the SO₂-treated coal system. The chromium (III) 2-ethylhexanoate catalyst showed doubled but still low activity with SO₂-treated compared with untreated coal. Nickel naphthenate showed much less variability in pyrene conversion with SO₂-treated coal than with the untreated coal. Both Molyvan-L and nickel octoate were active for pyrene hydrogenation when used with SO₂-treated Black Thunder coal, just as they were with the untreated Black Thunder coal.

The product distributions for pyrene hydrogenation given in Tables XII and XIII showed the pyrene primarily converted to dihydropyrene (DHP). In the case of the more active catalysts, tetrahydropyrene (THP) and hexahydropyrene (HHP) were formed in very small amounts.

The thermal reactions with these coals are also reported on Tables X-XII. In some instances, the addition of catalyst seemed to inhibit coal conversion compared to the thermal reaction. Chromium (III) 2-ethylhexanoate seemed to be the catalyst most detrimental to coal conversion.

Catalyst Selection for Coal Swelling Experiments

The following catalysts will be used for testing with swelled coals:

- Molybdenum naphthenate
- Molyvan-L
- Iron naphthenate
- Nickel octoate
- Cobalt naphthenate

The following catalyst precursors have been eliminated from the reaction schemes because of their performance and duplication of metal type:

- Chromium (III) 2-ethylhexanoate
- Nickel naphthenate
- Molybdenum octoate
- Vanadium naphthenate
- Cobalt 2-ethylhexanoate
- Iron 2-ethylhexanoate

Test of Reactivity of Swelled Coals

A coal swelling reactivity test was developed in order to provide a methodology by which to compare coal swelled by different solvents in the presence and absence of catalysts under both thermal and catalytic reaction conditions. The system used is described in Table XIV and is compared with the catalyst testing system used previously. The coal swelling reactivity test uses a solvent while the catalyst testing system did not. Three different solvents were chosen for the coal swelling reactivity test: 9,10-dihydroanthracene (DHA), 1-methylnaphthalene, and V1074, a coal-derived solvent from Wilsonville. The activity of the coal and pyrene in the coal swelling test system was measured by determining the amount of coal conversion with THF solubles and the amount of pyrene conversion with hydrogenated products.

To date, two solvents have been used: DHA and V1074. Two catalysts, Molyvan-L and nickel octoate, were used for both SO₂ and untreated Black Thunder coals. Cobalt naphthenate was also tested for the SO₂ and untreated Black Thunder coal with DHA, but it was not used with V1074 because of the low activity of cobalt naphthenate for both pyrene hydrogenation and coal conversion.

The pyrene and coal conversions obtained in the coal swelling reactivity test systems are presented in Tables XV and XVI (the former for the untreated Black Thunder coal and the latter for SO₂-treated Black Thunder coal).

In the case of untreated Black Thunder coal, the effect of the solvent on coal conversion was apparent. The presence of the hydrogen donor solvent, DHA, increased the amount of coal conversion compared with the V1074 solvent for equivalent reaction conditions. For example, when Molyvan-L was used as the catalyst, 89.7% coal conversion was obtained with DHA, while 84.7% was obtained with V1074. With nickel octoate a similar difference in coal conversion was observed: 87.0% with DHA and 81.5% with V1074. Pyrene conversion was higher with Molyvan-L than with nickel octoate but did not seem to be affected by the type of solvent present.

Conversion of the SO₂-treated Black Thunder coal was affected positively by the presence of DHA. The systems with Molyvan-L and nickel octoate yielded coal conversions of 92.4%. In V1074, however, the coal conversion of the SO₂-treated Black Thunder varied with the catalyst type, yielding 90.5% coal conversion with Molyvan-L and 82.1% coal conversion with nickel octoate. As with the untreated coal system, pyrene conversion with SO₂-treated coal did not seem to be affected much by the type of solvent present. The primary effect on pyrene conversion was the type of catalyst present. Molyvan-L yielded pyrene conversions of ~21%, while nickel octoate yielded pyrene conversions of 2 to 4%.

Cobalt naphthenate was used as a catalyst for both SO₂-treated and untreated Black Thunder coal with DHA as the solvent. Coal conversion with cobalt naphthenate was less than with either nickel octoate or Molyvan-L. The amount of pyrene conversion achieved was just slightly less than that achieved with nickel octoate.

Product distributions for pyrene hydrogenation in the DHA and V1074 solvents with untreated and SO₂-treated coals are given in Tables XV and XVI, respectively. The primary product formed was dihydropyrene (DHP), with trace amounts of tetrahydropyrene (THP) and hexahydropyrene (HHP) formed.

Planned Work

Research planned for the immediate future focuses on two areas:

(1) perform reactions using the coal swelling reactivity test system with 1-methylnaphthalene as the solvent and Molyvan-L and nickel octoate as the catalysts, and (2) develop a coal swelling methodology that will provide swelled feed coal for the swelled coal testing reaction system. The swelling experiments will consist of swelling the SO₂ and untreated Black Thunder coal with four different solvents: isopropanol, methanol, dimethylsulfoxide, and tetrahydrofuran. An additional solvent such as cresol or phenol may also be used. The procedure for swelling the coal that will be tried initially is (1) placing 2.0 g of maf coal in a bottle, (2) adding 10.0 g of solvent, (3) letting the coal sit for 24 hours, (4) measuring the swelling index, (5) filtering the solvent from the coal, (6) letting the coal surface dry, and (7) performing coal swelling test reactions.

Subtask 2.4: Bench-Scale Studies

The continuous feed two-stage reactor system, AU-51L, has been modified, flushed with coal-derived solvent, and tested to ensure proper control system operation. Experiments will be undertaken using raw and SO₂-treated Black Thunder subbituminous coal with and without coal swelling and catalyst impregnation.

Subtask 2.5: Solids Separation/Alternative Bottoms Processing

This subtask is being carried out by Foster Wheeler Development Corporation (FWDC). Their effort covers solids separation and alternative bottoms processing through direct delayed coking and the ASCOT process. The ASCOT process couples solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting troublesome solids within the coke drum. These results will then be integrated into the overall coal liquefaction concept.

The batch deasphalting screening tests continued through this quarter. The analysis of the feedstock (Wilsonville atmospheric residue) and the results of the screening tests are summarized in Tables XIX and XX, respectively. Figures 7 through 9 show the effect of temperature and solvent composition on the deasphalted oil (DAO) yield for three solvent categories.

Figure 7 indicates the effect of temperature on the DAO yield for the solvents that were deemed "too effective"--pentane, hexane, heptane, and xylene. Here, it is evident that the controlling variable is the type of solvent (i.e., paraffin or aromatic). The DAO yield was essentially independent of temperature and solvent/feed ratio. The yield averaged 61.3 wt% for the paraffin solvents and was 80.6 wt% for the single test with xylene. These numbers are consistent with the feedstock

characterization of 65.9 wt% oil (paraffin-soluble material) and 76.8 wt% soluble in toluene. None of these solvents provide the means for readily achieving lower yields and placing us in the 40 to 60 wt% DAO yield range we seek.

Figure 8 shows the effect of temperature on the DAO yield when using n-butane as the solvent. This was the first solvent that readily permitted the use of temperature as a controlling variable. Butane's solvent power, however, limits the maximum yield to about 50 wt% DAO. It must also be used over an undesirable temperature range, as is evident by its yield vs temperature curve. As the temperature is lowered from near the critical temperature (306°F), the DAO yield increases, peaks, and then falls off precipitously. This occurs in solvent deasphalting when the extraction temperature is reduced to the degree that the asphalt phase becomes too viscous for effective extraction. Potentially extractable material is then trapped in the asphalt.

It appeared that a blend of butane and a more effective paraffin solvent, used close to the critical temperature of butane, would be the best choice for producing a yield/temperature relationship of the proper sensitivity and also minimize the possibility of again encountering a too viscous asphalt phase. Pentane was selected as the blend component. The results, which are plotted in Figure 9, show a relationship that should be able to furnish the desired yield range.

Two more tests are planned to complete this task. A solvent blend at an 8/1 ratio and another at a 4/1 ratio with a higher percentage of pentane than yet tried. Sufficient data will be available to proceed with the transport tests.

CONCLUSIONS AND FUTURE WORK

Experimentation is confirming the validity of the process concept. Black Thunder subbituminous coal can be effectively beneficiated to about 4 wt% ash, and it is likely that it can be further treated to reduce the level to about 2 wt%. All three coals being studied are effectively swelled by a number of solvents. The most effective solvents are those having hetero-functionality. In addition, a synergistic effect has been demonstrated, in which solvent blends are more effective than the pure solvents alone. Therefore, it will be necessary to use only low levels of swelling agents and yet promote the impregnation of catalyst precursors. The choice of a solvent system for the deasphalting process is nearing completion, and bottoms stream transport tests should soon get under way.

ACKNOWLEDGEMENTS

This work is being supported by the United States Department of Energy under Contract DE-AC22-91PC91051. Appreciation is particularly extended to Mr. C. Gutterman of Foster Wheeler Development Corporation, Dr. C. W. Curtis of Auburn University, and Dr. S. Chander of Pennsylvania State University for participating in this program.

TABLE I
COAL SWELLING REPRODUCIBILITY TESTS

Solvent	Coal Swelling Ratio, Q		
	Black Thunder Subbituminous	Burning Star Illinois No. 6	Martin Lake Lignite
Cyclohexane:			
Operator 1	1.00	1.00	1.00
	1.00	1.04	1.01
Operator 2	1.00	1.00	1.00
	1.00	1.00	1.00
Average	1.00	1.01	1.00
Std Dev	--	0.02	0.005
Methanol:			
Operator 1	1.23	1.20	1.25
	1.32	1.19	1.25
Operator 2	1.37	1.21	1.27
	1.35	1.24	1.44
Average	1.32	1.21	1.30
Std Dev	0.06	0.02	0.09
Tetrahydrofuran:			
Operator 1	1.69	1.55	1.32
	1.72	1.66	1.35
Operator 2	1.54	1.69	1.41
	1.52	1.57	1.34
Average	1.62	1.62	1.36
Std Dev	0.10	0.07	0.04
Tetrabutylammonium Hydroxide:			
Operator 1	2.39	2.12	2.73
	2.65	2.13	2.94
Operator 2	2.22	2.15	2.79
	2.68	2.21	2.53
Average	2.48	2.15	2.75
Std Dev	0.22	0.04	0.17

TABLE II
SWELLING REPRODUCIBILITY TESTS FOR MIXTURES

Solvent	Coal Swelling Ratio, Q		
	Black Thunder Subbituminous	Burning Star Illinois No. 6	Martin Lake Lignite
Tetralin:			
	1.04	1.01	1.03
	1.04	1.00	1.03
Average	1.04	1.01	1.03
Tetralin/ Isopropanol:2/1:			
	1.48	1.46	1.35
	1.69	1.52	1.37
	1.47	1.44	1.28
	1.46	1.48	1.27
Average	1.52	1.48	1.32
Std Dev	0.11	0.03	0.05
Tetralin/ Isopropanol:1/2:			
	1.52	1.43	1.32
	1.54	1.42	1.34
	1.59	1.38	1.38
	1.64	1.32	1.35
Average	1.57	1.39	1.35
Std Dev	0.05	0.05	0.03
Isopropanol:			
	1.38	1.17	1.26
	1.44	1.18	1.24
	1.37	1.17	1.29
	1.41	1.12	1.29
Average	1.40	1.16	1.27
Std Dev	0.03	0.03	0.02

TABLE III
SWELLING RATIO OF COAL/SOLVENT BLENDS
 (325 Mesh Coal with 1 ml Winthrobe Tubes)

Solvent/Time	Black Thunder		Illinois No. 6		Martin Lake Lignite	
	24 Hr	96 Hr	24 Hr	96 Hr	24 Hr	96 Hr
Hexane	--	1.01	--	1.00	--	0.95
Cyclohexane	--	1.00	1.00	1.00	--	--
Benzene	--	1.12	--	1.06	--	1.14
Toluene	--	1.04	--	1.16	--	1.00
Xylene	--	1.02	--	1.04	--	1.05
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Methanol	1.28	1.35	1.16	1.23	1.43	1.36
Ethanol	--	1.31	--	1.26	--	1.24
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
33% Tetralin/67% IPA	1.40	1.53	1.31	1.43	1.18	1.37
67% Tetralin/33% IPA	1.39	1.47	1.34	1.49	1.18	1.36
80% Tetralin/20% IPA	1.34	1.42	1.22	1.35	1.10	1.23
90% Tetralin/10% IPA	1.22	1.35	1.13	1.19	1.10	1.18
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Cresol	1.16	1.29	1.28	1.48	1.13	1.20
Acetone	--	1.32	--	1.24	--	1.25
Methyl Ethyl Ketone	1.1	1.34	1.29	1.29	1.27	1.3
Methyl Acetate	1.28	1.34	1.20	1.20	1.25	1.25
Tetrahydrofuran	1.45	1.53	1.50	1.63	1.36	1.38
Chloroform	--	1.17	--	1.19	--	1.03
Chlorobenzene	1.08	1.08	1.07	1.16	1.09	1.12
Nitrobenzene	1.11	1.15	1.18	1.19	1.08	1.11
Aniline	1.41	1.64	1.71	1.94	1.12	1.19
Tetrabutylammonium Hydroxide	2.05	2.45	1.59	2.18	2.04	2.66
Dimethyl Sulfoxide	2.19	2.39	2.08	2.15	1.52	1.63

TABLE IV
SWELLING RATIO OF THREE SAMPLES OF BLACK THUNDER COAL
(10 ml Centrifuge Tubes)

Solvent/Time	Untreated -325 Mesh					Untreated 8 x 60 Mesh					SO ₂ -Treated 8 x 60 Mesh				
	2 Hr	4 Hr	24 Hr	96 Hr		2 Hr	4 Hr	24 Hr	96 Hr		2 Hr	4 Hr	24 Hr	96 Hr	
Isopropanol 50X IPA/50X H ₂ O	--	--	--	--		1.20	--	1.25	--		1.27	--	1.42	--	
	--	--	--	1.38		--	--	--	--		--	--	1.40	1.40	
20X IPA/80X Tetralin	1.16	--	1.24	--		1.25	--	1.48	--		1.33	1.38	1.41	1.41	
20X IPA/50X Toluene	--	--	--	--		1.18	--	1.21	--		1.26	--	1.42	--	
30X IPA/70X Toluene	--	--	--	--		1.20	--	1.24	--		1.38	--	1.51	--	
40X IPA/60X Toluene	--	--	--	--		1.18	--	1.30	--		1.32	--	1.56	--	
Methanol (repeat)	1.34	1.43	1.43	--		--	--	1.26	1.26		1.24	--	--	--	
70X MeOH/30X H ₂ O	--	--	1.19	1.33		--	--	--	--		1.18	--	--	--	
50X MeOH/50X H ₂ O	--	--	1.32	1.40		1.24	--	1.24	--		--	--	1.25	--	
30X MeOH/70X H ₂ O	--	--	1.38	1.36		--	--	--	--		--	--	1.21	--	
	--	--	1.21	1.28		--	--	--	--		--	--	--	--	
25X MeOH/75X Tetralin	1.43	1.46	1.49	--		--	--	--	--		--	--	--	--	
Acetone	--	--	--	--		1.23	--	1.24	--		1.52	--	1.52	--	
Tetrahydrofuran 70X THF/30X H ₂ O	--	--	1.42	1.55		--	--	1.54	1.59		1.83	1.94	2.07	2.08	
50X THF/50X H ₂ O	--	--	1.87	1.91		1.71	--	1.86	--		1.93	--	2.15	--	
30X THF/70X H ₂ O	--	--	1.78	1.85		--	--	--	--		--	--	--	--	
20X THF/80X H ₂ O	--	--	1.52	1.60		1.36	--	1.49	--		1.43	--	1.52	--	
10X THF/90X H ₂ O	1.40	1.46	1.46	--		--	--	--	--		--	--	--	--	
5X THF/95X H ₂ O (repeat)	1.24	1.24	1.31	--		--	--	--	--		--	--	--	--	
	1.40	1.38	1.41	--		1.14	--	1.16	--		1.16	--	1.16	--	
Aniline (repeat)	--	--	--	--		1.17	--	1.37	--		1.22	--	1.68	--	
	--	--	--	--		--	--	--	--		1.21	--	1.97	--	
Dimethyl Sulfoxide 10X DMSO/90X Tetralin	2.05	2.37	2.37	2.37		1.60	--	2.09	--		2.28	2.35	2.41	2.58	
5X DMSO/95X Tetralin	1.39	1.49	1.58	--		1.21	--	1.60	--		1.41	--	1.83	--	
	1.19	1.27	1.32	--		1.13	--	1.43	--		1.23	--	1.44	--	

TABLE V

REACTION CONDITIONS

Temperature	426°C
Time	30 minutes
Pyrene Charge	1.5 g
Coal	Illinois No. 6
Resid	Maya
Solvent	None
Pressure	1250 psig H ₂ at ambient temperature
Catalyst Loading	600-800 ppm on feed basis
Analysis	GC of pyrene and pyrene hydrogenation products; coal conversion

DCC/ml/92839
12/15/92

TABLE VI
PRODUCT DISTRIBUTIONS OF PYRENE
WITH ADDED COAL AND MOLYBDENUM NAPHTHENATE

Mo Naphthenate (ppm)	Added Component	Product Distribution, mole%					
		PYR	DHP	THP	HHP1	HHP2	HHP3
679	None	89.0	11.0	0.0	0.0	0.0	0.0
709	None	92.7	7.3	0.0	0.0	0.0	0.0
655	Coal (6.4%)	78.4	19.6	1.1	0.0	0.0	0.9
700	Coal (6.4%)	75.2	22.5	1.5	0.0	0.0	0.8
896	Coal (8.9%)	75.0	22.6	1.7	0.0	0.7	0.0
681	Coal (9.0%)	74.6	22.9	1.7	0.0	0.8	0.0
466	Coal (11.9%)	66.9	30.0	3.1	0.0	0.0	0.0
648	Coal (11.7%)	72.6	24.8	1.8	0.0	0.0	0.8
1131	Coal (19.1%)	61.4	32.8	4.5	0.7	0.0	0.6
511	Coal (19.3%)	62.0	32.5	4.4	0.6	0.0	0.5

PYR - pyrene
 DHP - dihydroxyrene
 THP - 4,5,9,10-tetrahydroxyrene
 HHP1 - 1,2,3,3A,4,5-hexahydroxyrene
 HHP2 - 1,2,3,6,7,8-hexahydroxyrene
 HHP3 - hexahydroxyrene isomer

DCC/ml/92839
 12/15/92

TABLE VII
PRODUCT DISTRIBUTIONS OF PYRENE
WITH ADDED COAL AND MOLYVAN-L

Molyvan-L (ppm)	Added Component	Product Distribution, mole%					
		PYR	DHP	THP	HHP1	HHP2	HHP3
607	None	81.6	15.6	0.0	0.7	1.2	0.9
717	None	87.0	11.6	0.0	0.0	0.6	0.8
564	None	82.1	17.9	0.0	0.0	0.0	0.0
701	None	93.8	5.1	0.0	0.0	0.0	1.1
547	Coal (6.4%)	78.4	20.0	1.0	0.0	0.0	0.6
549	Coal (6.3%)	78.7	19.4	1.0	0.0	0.0	0.9
510	Coal (9.1%)	75.0	22.0	2.1	0.0	0.0	0.9
613	Coal (8.9%)	74.1	23.4	1.7	0.0	0.0	0.8
447	Coal (13.5%)	69.7	27.6	2.7	0.0	0.0	0.0
607	Coal (13.3%)	70.4	26.7	2.1	0.0	0.0	0.8
577	Coal (19.1%)	61.9	32.6	4.3	0.5	0.0	0.7
504	Coal (19.3%)	61.8	32.5	4.3	0.6	0.0	0.7

PYR = pyrene
DHP = dihydroxyrene
THP = 4,5,9,10-tetrahydroxyrene
HHP1 = 1,2,3,3A,4,5-hexahydroxyrene
HHP2 = 1,2,3,6,7,8-hexahydroxyrene
HHP3 = hexahydroxyrene isomer

DCC/ml/92839
12/15/92

TABLE VIII
COAL AND PYRENE CONVERSION IN REACTIONS
WITH MOLYBDENUM NAPHTHENATE AND MOLYVAN-L

	Added Coal			
Catalyst (ppm)	(g)	wt%	Pyrene Conversion (mol%)	Coal Conversion (wt%)
Mo-Naph:				
665	0.1221	6.4	21.6	98.5
770	0.1219	6.4	24.8	91.7
1131	0.4537	19.1	38.6	88.5
511	0.4524	19.3	38.0	88.5
Moly-L:				
547	0.1226	6.4	21.6	92.5
549	0.1201	6.3	21.3	98.1
577	0.4487	19.1	38.1	88.4
504	0.4525	19.3	38.2	89.7

Mo-Naph = molybdenum naphthenate

Moly-L = Molyvan-L

DCC/ml/92839
12/15/92

TABLE IX

PROXIMATE AND ULTIMATE ANALYSIS OF BLACK THUNDER
AND SO₂-TREATED BLACK THUNDER COALS*

	Proximate Analysis			
	Black Thunder		SO ₂ Treated Black Thunder	
	As Received	Dry Basis	As Received	Dry Basis
% Moisture	11.20		9.88	
% Ash	5.43	6.12	3.08	3.42
% Volatile	44.53	50.15	41.74	46.32
% Fixed Carbon	38.84	43.73	45.30	50.26
Total	100.00	100.00	100.00	100.00
Btu/lb	10606	11944	10993	12198
% Sulfur	0.39	0.44	0.73	0.81
maf Btu		12723		12630
	Ultimate Analysis			
	Black Thunder		SO ₂ Treated Black Thunder	
	As Received	Dry Basis	As Received	Dry Basis
% Moisture	11.20		9.88	
% Carbon	61.87	69.67	63.57	70.54
% Hydrogen	4.33	4.88	4.46	4.95
% Nitrogen	0.81	0.91	0.80	0.89
% Sulfur	0.39	0.44	0.73	0.81
% Ash	5.43	6.12	3.08	3.42
% Oxygen (diff)	15.97	17.98	17.48	19.39

*Commercial Testing and Engineering Co., Birmingham, Alabama, laboratory.

TABLE X
PYRENE AND COAL CONVERSION
FOR UNTREATED BLACK THUNDER COAL

Catalyst	(ppm)	Added Coal wt%	Pyrene Conversion (mole%)	Coal Conversion (wt%)
Mo Naphthenate	652	19.1	2.2	49.4
	625	19.1	4.6	46.9
Molyvan L	710	19.2	20.1	72.9
	622	20.1	28.2	68.3
	574	20.1	20.4	77.5
Fe Naphthenate	744	20.0	1.3	62.1
	666	20.0	1.5	46.3
Ni Naphthenate	687	19.9	12.5	56.6
	519	20.1	4.3	51.5
	795	19.9	15.2	66.6
	693	20.0	20.5	76.0
Ni Octoate	697	20.1	25.5	78.0
	638	20.1	25.7	69.5
Cr(III)2- ethylhexanoate	714	20.1	1.1	58.6
	660	20.1	1.6	48.2
	731	20.1	0.8	45.5
	674	20.1	1.3	39.7
Va Naphthenate	653	19.8	4.2	64.4
None	0	20.3	1.5	58.9
	0	20.3	1.7	60.2

TABLE XI
PYRENE AND COAL CONVERSIONS FOR SO₂-TREATED BLACK THUNDER COAL

Catalyst	(ppm)	Added Coal wt%	Pyrene Conversion (mole%)	Coal Conversion (wt%)
Mo Naphthenate	572	19.9	23.4	83.5
	556	19.9	28.1	87.5
	668	19.8	27.3	86.1
Molyvan L	585	19.9	26.0	90.2
	742	19.9	30.0	90.4
Fe Naphthenate	731	21.4	7.8	65.4
	651	21.5	1.9	61.4
Ni Naphthenate	609	21.5	15.5	69.9
	605	21.5	16.1	77.9
Ni Octoate	781	19.9	23.3	79.0
	762	19.9	20.5	89.7
Cr(III)2- ethylhexanoate	659	19.9	2.1	53.7
	736	19.8	4.4	55.8
Va Naphthenate	633	19.6	3.4	67.4
	646	19.7	4.4	64.8
None	0	20.1	1.6	65.6
	0	20.1	1.0	49.4

TABLE XII

PRODUCT DISTRIBUTION FROM PYRENE HYDROGENATION REACTIONS
IN THE PRESENCE OF UNTREATED BLACK THUNDER COAL

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole%)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Mo Naphthenate	652	0.7 (19.1)	97.8	2.2	0	0	0	0
	625	1.5 (19.1)	95.4	4.6	0	0	0	0
Molyvan L	710	7.3 (19.2)	79.9	19.0	0.4	0	0	0.7
	622	7.4 (20.1)	71.8	26.3	1.2	0	0	0.7
	574	10.3 (20.1)	79.6	19.2	0.6	0	0	0.6
Fe Naphthenate	744	0.8 (20.0)	98.7	0.8	0	0	0	0.5
	666	1.2 (20.0)	98.5	0.5	0	0	0	1.0
Ni Naphthenate	687	4.4 (19.9)	87.5	12.1	0	0	0	0.4
	795	5.4 (19.9)	84.8	14.7	0	0	0	0.5
	693	7.4 (20.0)	79.5	19.4	0.6	0	0	0.5
Ni Octoate	697	9.1 (20.1)	74.5	24.0	1.0	0	0	0.5
	638	9.1 (20.1)	74.3	24.4	1.0	0	0	0.3
Cr(III)2- ethyl hexanoate	714	0.7 (20.1)	98.9	0.7	0	0	0	0.4
	660	1.0 (20.1)	98.4	1.0	0	0	0	0.6
	731	0.6 (20.1)	99.2	0.3	0	0	0	0.5
Va Naphthenate	653	2.0 (19.8)	95.8	3.4	0	0	0	0.8
None	0	0.9 (20.3)	98.5	0.8	0	0	0	0.7
	0	1.0 (20.3)	98.3	1.1	0	0	0	0.6

PYR = pyrene
 DHP = dihydropyrene
 THP = tetrahydropyrene
 HHP1, HHP2, HHP3 = isomers of hexahydropyrene
 % HYD = hydrogenation

TABLE XIII

PRODUCT DISTRIBUTION FROM PYRENE HYDROGENATION REACTIONS
IN THE PRESENCE OF SO₂-TREATED BLACK THUNDER COAL

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Mo Naphthenate	572	8.1 (19.9)	76.6	22.4	1.0	0	0	0
	556	9.6 (19.9)	71.9	26.2	1.3	0	0	0.6
	668	9.8 (19.8)	72.7	25.9	0.7	0	0	0.7
Molyvan L	585	8.9 (19.9)	74.0	25.2	0.8	0	0	0
	742	10.6 (19.9)	70.0	28.2	1.8	0	0	0
Fe Naphthenate	731	3.2 (21.4)	92.2	6.9	0	0	0	0.9
	651	1.0 (21.5)	98.1	1.4	0	0	0	0.5
Ni Naphthenate	609	5.6 (21.5)	84.5	14.9	0	0	0	0.6
	605	5.7 (21.5)	83.9	15.6	0	0	0	0.5
Ni Octoate	781	8.3 (19.9)	76.7	22.2	0.6	0	0	0.5
	762	7.3 (19.9)	79.5	19.5	0.5	0	0	0.5
Cr(III)2-ethylhexanoate	659	1.1 (19.9)	97.9	1.4	0	0	0	0.7
	736	1.9 (19.8)	95.6	3.8	0	0	0	0.6
Va Naphthenate	633	1.7 (19.6)	96.6	2.6	0	0	0	0.8
	646	2.1 (19.7)	95.6	3.5	0	0	0	0.9
None	0	1.0 (20.1)	98.4	0.9	0	0	0	0.7
	0	0.6 (20.1)	99.0	0.5	0	0	0	0.5

PYR = pyrene
 DHP = dihydroxyrene
 THP = tetrahydroxyrene
 HHP1, HHP2, HHP3 = isomers of hexahydroxyrene
 % HYD = hydrogenation

TABLE XIV
CATALYST SCREENING AND COAL SWELLING REACTIVITY TEST SYSTEMS

Parameters	Catalyst Screening Test System	Coal Swelling Test System
Temperature	410°C	410°C
Pressure	1250 psig H ₂ at ambient temperature	1250 psig H ₂ at ambient temperature
Time	30 minutes	30 minutes
Coal	0.375 g maf SO ₂ or untreated Black Thunder Coal	1.33 g maf SO ₂ or untreated Black Thunder Coal
Pyrene	1.5 g	0.67 g
Solvent	No solvent	2.00 g of either 9,10-dihydroanthracene, V1074 from Wilsonville or 1-methylnaphthalene
Catalyst Loading Catalysts	600-700 ppm (based on feed) Molyvan L molybdenum naphthenate iron naphthenate nickel octoate cobalt naphthenate chromium III 2-ethylhexanoate nickel naphthenate molybdenum octoate vanadium naphthenate cobalt 2-ethylhexanoate iron 2-ethylhexanoate	600-700 ppm (based on feed) Molyvan L, nickel octoate cobalt naphthenate

TABLE XV

PYRENE AND COAL CONVERSIONS FOR UNTREATED BLACK THUNDER COAL

Catalyst Type	Catalyst Loading (ppm)*	Added Coal (wt%)	Pyrene Conversion (mole %)	Coal Conversion (wt%)
Solvent: 9,10-dihydroanthracene				
Molyvan-L	693	30.5	18.4	89.8
	660	30.5	12.0	89.5
Nickel Octoate	576	30.7	5.1	85.8
	554	30.6	3.6	88.2
Cobalt Naphthenate	654	30.4	2.0	83.1
	648	30.5	2.3	83.3
Solvent: V1074				
Molyvan-L	664	30.3	12.9	85.4
	639	30.2	16.8	84.0
Nickel Octoate	647	30.6	1.9	82.3
	730	30.5	10.1	80.6
	650	30.6	8.5	81.7

*Based on feed.

DCC/ml/92839
12/15/92

TABLE XVI
PYRENE AND COAL CONVERSIONS FOR SO₂-TREATED BLACK THUNDER COAL

Catalyst Type	Catalyst Loading (ppm)*	Added Coal (wt%)	Pyrene Conversion (mole %)	Coal Conversion (wt%)
Solvent: 9,10-dihydroanthracene				
Molyvan-L	674	31.3	23.9	92.9
	634	31.3	17.7	91.9
Nickel Octoate	675	31.4	2.7	95.9
	652	31.4	4.7	88.8
Cobalt Naphthenate	602	31.3	2.4	86.4
	613	31.2	3.0	85.3
Solvent: V1074				
Molyvan-L	598	31.4	18.9	88.5
	638	31.4	23.2	92.2
Nickel Octoate	618	31.0	20.3	90.9
	864	31.0	3.9	84.2
	667	31.4	0.0	79.9

*Based on feed.

DCC/ml/92839
12/15/92

TABLE XVII

**PRODUCT DISTRIBUTIONS FROM PYRENE HYDROGENATION
IN PRESENCE OF UNTREATED BLACK THUNDER COAL**

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Solvent: 9,10 dihydroanthracene								
Molyvan L	693	6.6 (30.5)	81.6	17.4	0.5	0	0	0.5
	660	4.1 (30.5)	88.0	11.6	0.4	0	0	0
Nickel Octoate	576	2.3 (30.7)	94.9	4.3	0	0	0	0.8
	554	1.8 (30.6)	96.4	2.7	0	0	0	0.9
Cobalt Naphthenate	654	1.2 (30.4)	98.0	1.0	0.5	0	0	0.5
	648	1.3 (30.5)	97.7	1.3	0.5	0	0	0.5
Solvent: V1074								
Molyvan L	664	4.9 (30.3)	87.1	11.7	0.6	0	0	0.6
	639	6.4 (30.2)	83.2	15.2	0.8	0	0	0.8
Nickel Octoate	647	0.6 (30.6)	98.1	1.9	0	0	0	0
	730	3.6 (30.5)	89.9	9.3	0.8	0	0	0
	650	3.0 (30.6)	91.5	8.0	0.5	0	0	0

PYR = pyrene
 DHP = dihydropyrene
 THP = tetrahydropyrene
 HHP1, HHP2, HHP3 = isomers of hexahydropyrene
 % HYD = hydrogenation

TABLE XVIII

PRODUCT DISTRIBUTIONS FROM PYRENE HYDROGENATION
IN THE PRESENCE OF SO₂-TREATED BLACK THUNDER COAL

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Solvent: 9,10 dihydroanthracene								
Molyvan L	674	8.5 (31.3)	76.1	22.5	1.4	0	0	0
	634	6.3 (31.3)	82.3	16.6	1.1	0	0	0
Nickel Octoate	675	1.4 (31.4)	97.3	1.9	0	0	0	0.8
	652	2.1 (31.4)	95.3	3.9	0	0	0	0.8
Cobalt Naphthenat e	602	1.4 (31.3)	97.6	1.2	0.6	0	0	0.6
	613	1.8 (31.2)	97.0	1.5	0.7	0	0	0.8
Solvent: V1074								
Molyvan L	598	6.8 (31.4)	81.1	18.1	0	0	0.8	0
	638	8.3 (31.4)	76.8	21.5	1.7	0	0	0
	618	7.8 (31.0)	79.7	18.0	1.5	0	0	0.8
Nickel Octoate	864	1.3 (31.0)	96.1	3.9	0	0	0	0
	667	0.0 (31.4)	100.0	0	0	0	0	0

PYR - pyrene
 DHP - dihydropyrene
 THP - tetrahydropyrene
 HHP1, HHP2, HHP3 - isomers of hexahydropyrene
 % HYD - hydrogenation

TABLE XIX
FEEDSTOCK INSPECTIONS:
WILSONVILLE ATMOSPHERIC RESIDUE⁽¹⁾

FW Identification No.	22777
Specific Gravity @ 60/60°F	1.187
Asphaltenes, ⁽²⁾ wt%	10.9
Toluene Insolubles, wt%	23.2
Quinoline Insolubles, wt%	22.2
Ash, wt%	11.49
Softening Point (R&B), °F	124
Conradson Carbon Residue, wt%	38.1
Sulfur, wt%	1.40
Carbon, wt%	77.6
Hydrogen, wt%	7.4
Metals, ppm:	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM Distillation (D-1160), °F ⁽³⁾	
IBP	634
2 vol%	704
5	765
10	810
20	858
30	900
40	975
41	⁽⁴⁾

- (1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal.
(2) Asphaltenes Precipitation with Normal Heptane, Method IP143.
(3) Corrected to atmospheric pressure.
(4) Cracking at still temperature of 650°F.

TABLE XX

SUMMARY OF BATCH DEASPHALTING TEST RESULTS

Run No.	Solvent	S/F Ratio V/V @ 60°F	Temp, °F	Yields, wt%			Ash, wt%	
				Oil	Asphalt	Recovery	Oil	Asphalt
3015	Heptane	8	475	60.4	32.0	92.4	0.010	27.75
3016	Heptane	8	500	58.5	30.5	89.0	0.006	27.23
3018	Heptane	4	500	60.6	35.8	96.4	0.030	27.85
3019	Heptane	8	520	60.9	28.8	89.7	0.060	28.44
3020	Heptane	8	550	65.3	40.3	105.6	0.024	28.00
3017	Xylene	8	565	80.6	25.3	105.9	2.27	33.06
3021	Hexane	4	430	59.8	33.7	93.5	0.017	30.70
3022	Pentane	4	380	63.6	35.7	99.3	0.020	26.00
3023	Butane	4	290	32.5	69.8	102.3	0.017	15.88
3024	Butane	4	240	30.4	68.4	98.8	0.006	17.04
3025	Butane	4	265	49.5	52.5	102.0	0.0044	20.33
3026	80% C ₄ /20% C ₅	4	290	47.9	49.4	97.3	0.0037	21.51
3027	70% C ₄ /30% C ₅	4	290	50.0	47.0	97.0	0.0053	23.77
3028	50% C ₄ /50% C ₅	4	290	54.0	46.3	100.3	0.0055	25.63

S/F ratio = solvent/feed ratio.

DCC/ml/92839
12/15/92

Figure 1

Equilibrium Swelling Ratio Versus Dipole Moment

Figure 2
Swelling Ratios of 325-mesh Coal with the IPA/Tetralin System

Figure 3
Swelling Ratios of 325-mesh Black Thunder Coal
with the THF/Water System

Figure 4
Swelling Ratios of 325-mesh Black Thunder Coal
with the Methanol/Water System

Figure 5
Swelling Ratios of 325-mesh Black Thunder Coal with Solvent Blends

Figure 6
Swelling Rates of 325-mesh Black Thunder Coal

FIGURE 7

EFFECT OF TEMPERATURE ON DAO YIELD

FIGURE 8

EFFECT OF TEMPERATURE ON DAO YIELD FOR N-BUTANE

FIGURE 9

EFFECT OF BUTANE/PENTANE FEED COMPOSITION
ON DAO YIELD

APPENDIX A

DISPERSED CATALYSTS IN COAL LIQUEFACTION: A LITERATURE AND PATENT REVIEW

**DISPERSED CATALYSTS IN COAL LIQUEFACTION:
A LITERATURE AND PATENT REVIEW**

1. INTRODUCTION

1.1 Objectives and scope

This review reports on a literature and patent survey on the use of dispersed (unsupported) catalysts in coal liquefaction. It is in support of the overall goal of the DOE contract on "Advanced Coal Liquefaction Concepts" to identify an effective dispersed catalyst process for low-rank subbituminous coal and lignite. This review was conducted to provide leads on effective dispersion techniques and catalytic components, and to summarize the current understanding on the mechanisms for catalysis, particularly by Fe and Mo.

Several reviews on the general area of coal liquefaction catalysts have excellent discussions on dispersed catalysts. Among these are those of Derbyshire (1988)¹ and Charcosset and Genard (1987)²; the latter cites other literature reviews, such as the review of Narain, et. al. (1987)³ which concentrated on iron-based dispersed catalysts. This review updates these previous ones with recent developments in both process and fundamental studies, particularly in catalyst dispersion methods and characterization of catalyst activity. Most of the recent work addresses these previous reviews' recommended work in these areas of research. Although there is an emphasis on catalysis by molybdenum and iron in this review, other dispersed catalysts reported in both the patent and open literature are also surveyed.

It is also to be noted that dispersed catalysts were the original coal liquefaction catalysts used by the Germans, who did a lot of developmental work which led to embarking on a commercialization program as early as 1925. Literature abstracting services do not go as far back as this. Donath (1982)⁴ provides both a good review of this early history and

references to key patents and publications summarizing the early work. However, the importance of this early work is not and cannot be ignored. This review provides a brief discussion of the importance of this early work, which also laid the foundation for later work on the transition metal sulfides as petroleum hydroprocessing catalysts. This review also discusses some recent developments in this field that are relevant to our current interest in coal liquefaction dispersed catalysts. Interestingly, the original pre-World War II interest in these catalysts has now gone full-circle. Although active catalysts have been identified and recent progress in analytical techniques have allowed better catalyst characterization, the basis and origin of catalytic activity is still little understood.

Although every effort at an exhaustive search has been made, this review is by no means complete. A computerized search on the field was performed using the keywords "dispersed, slurry, catalysts, coal, liquefaction". It is possible that some of the relevant literature were indexed under other keywords. In most cases, references for a researcher's or research group's work are confined only to selected, more contemporary articles or to those considered key articles for that particular researcher or group.

Finally, no attempt is made to compare catalysts studied by different researchers or groups, other than in general terms. In addition to variations in experimental conditions, the lack of standardization, particularly in product work-up and characterization, precludes any meaningful ranking of catalyst performance. Any comparisons presented in this review will be of catalysts prepared and/or tested by the same researcher or group.

1.2 Catalysis in coal liquefaction

In conventional coal liquefaction, hydrogen is added to coal using catalyst at elevated pressure and temperature. Although there is overlap to some extent, liquefaction is generally regarded to proceed via two consecutive steps: coal dissolution primarily by depolymerization followed

by upgrading via molecular weight reduction and heteroatom removal.¹ Liquefaction has been conducted in a single stage or in stages,⁵ with the same or different catalysts in each stage.

The emphasis of this review will be on catalysis in conventional coal liquefaction. However, pertinent literature in processes such as pyrolysis (the first step in liquefaction), hydrolysis, and coal/residuum coprocessing will also be cited.

1.2.1 Liquefaction catalysts

Derbyshire's (1988)¹ discussion of catalysis in coal liquefaction is based on the broad categories of dispersed and supported (or heterogeneous) catalysts. The terms slurry, disposable, soluble, homogeneous, or once-through have been used synonymously with "dispersed" in the literature. Dispersed catalysts are usually used as dissolution catalysts while supported catalysts are primarily for hydrotreating. There can be overlaps in these categories and functions. For example, supported catalysts when ground and added as fine powder to coal can be considered as slurry catalysts. A pulverized catalyst containing a transition metal compound supported on sepiolite, palygorskite, or attapulgite has been claimed as a coal liquefaction slurry catalyst.⁶ Some dispersed catalysts can have both dissolution and upgrading functionalities, such as multicomponent catalyst systems.

Based on the requisite dissolution and upgrading steps during coal liquefaction, a desirable liquefaction catalyst must possess activities for:

- 1) hydrogenation of polycyclic aromatic compounds,
- 2) cleavage of C-C or C-O bonds through hydrocracking reactions, and
- 3) desulfurization and denitrogenation.

The development of such a catalyst is driven by the cost reduction incentives associated with increasing hydrogen utilization efficiency and reducing capital and operating costs by lowering reaction severity. These

cost reductions may be substantial to offset the possibly higher cost of a dispersed catalyst.

1.2.2 Catalyst mechanisms for liquefaction

During pyrolysis (or liquefaction without a solvent), it is reasonable to assume that liquefaction occurs only in the vicinity of the catalyst; in which case, the catalytic action is associated with cleaving coal linkages and hydrogenation. The catalyst and H_2 also suppress cross-linking or retrogressive reactions. In this case, a high degree of dispersion and/or mobility of the catalyst is important.

During liquefaction with a H-donor solvent, there are three possible pathways for hydrogen transfer to the coal:

- 1) Direct hydrogenation -- the catalyst can promote direct reaction of hydrogen (probably in the form of dissociatively adsorbed H_2) with the coal, thus effectively reducing the requirement for hydrogen donation from the solvent.
- 2) Hydrogen transfer from the solvent -- the catalyst can generate or regenerate the solvent H-donors by reaction with H_2 . Since liquefaction can occur even in the absence of a solvent, this pathway does not appear to be the only one operative during liquefaction.
- 3) Hydrogen transfer from other H donors -- although the generation of H-donating groups in coal can also occur thermally, this can be enhanced by addition of a catalyst.

For a given coal and set of reaction conditions, the competition among these pathways is affected by the catalyst activity and solvent composition, which can also be interdependent.¹ Derbyshire's (1988) review¹ has a good summary of proposed mechanisms for liquefaction, e.g.,

solvent-mediated hydrogenolysis and radical hydrogen transfer mechanisms for hydrogenation catalysts.

The role of dispersed catalysts during the initial stages of liquefaction when retrogressive reactions can take place, especially in low-rank coals, has been actively investigated, particularly with respect to altering initial reaction pathways. Dispersed iron catalysts have been researched extensively by DOE-sponsored programs but the question on how iron catalyzes initial reactions has remained unanswered. The mechanisms for catalysis by Fe and Mo have also been studied and this review will present results from recent work in later sections.

1.3 Dispersed catalysts

Although there has been a dramatic increase in interest in dispersed catalysts for coal liquefaction in recent years, these catalysts were originally used in the primary step of brown coal liquefaction in the Bergius-Pier process developed in Germany. In this process, coal is hydrogenated in the liquid phase at elevated pressure and temperature with a dispersed catalyst; the liquid from this primary stage is then hydrogenated over supported catalyst in the second stage. In addition to a commercialization program, the Germans also had a catalyst development program. This section will briefly discuss some of the milestones in that program; there will also be a brief discussion of coal minerals, ores, and manufacturing residues as disposable catalysts.

1.3.1 Early developments

Donath (1982)⁴ reviews the history of the German developments in coal liquefaction. Using cresylic acid as a coal tar model compound, Pier and others determined that sulfides and oxides of Mo, W, and Co, and sulfides of Fe were active sulfur-resistant hydrogenation catalysts at 200 bar H₂ (2900 psi). This study was extended to brown coal tar with testing of nearly all elements singly or in combination, with limited testing of

noble metals because of cost and availability considerations. Mo and W and Groups V and VI elements were the most active catalysts, using conversion to gasoline as criterion. The combinations of molybdic acid/zinc oxide/magnesia and molybdic/chromic acids were found to be effective as well. In the liquefaction of bituminous coal, tin in combination with HCl was found to be active. Later work with bituminous coal at 600 bar H_2 (8700 psi) using an iron catalyst demonstrated similar performance. The results from this early catalyst testing program were applied in the various commercial plants started up between 1927 and 1943; by 1944, there were a total of 12 plants with a combined motor fuel product capacity of about 4 million metric tons per year. Table 1, adapted from Donath⁴, shows the various hydrogenation plants and their feeds. It also shows the catalysts and pressures used in the primary liquefaction first stage. The catalysts used in the coal oil refining in the second stage evolved from a catalyst mixture of oxides of Mo, Zn, and Mg to WS_2 and combinations of these two catalysts. After 1940, the "workhorse" refining catalyst was WS_2 -NiS supported on alumina or WS_2 supported on montmorillonite earth.

The main drawback in the early work was the high catalyst concentrations required to obtain the refined products. For example, concentrations of 20-25% of the coal slurry of pulverized Mo-containing catalysts were used for brown coals whose high alkali content decreased Mo activity. Experiments with low Mo concentration were effective if the MoO_3 was supported. This then led to the development of supported catalysts which later impacted petroleum refining.

In the development of bituminous coal liquefaction, the use of high pressure, i.e. 600-700 bar (8700-10,155 psi) vs. 200-300 bar (2900-4350 psi) for brown coal, gave satisfactory performance with low-cost catalysts such as iron compounds impregnated on to coal or to char. The main iron catalyst was an iron-oxide-containing residue of aluminum production from bauxite (Bayer Masse or red mud). Ferrous sulfate was also used.

1.3.2 Disposable catalysts

In the development of the Bergius-Pier liquefaction process, the advantage of a disposable catalyst was recognized, i.e., no catalyst aging/recovery concern and low catalyst cost. This was also recognized in the modern SRC-II process which used finely-divided coal minerals as catalysts. The beneficial effects of mineral matter in coal liquefaction have been investigated extensively; Narain, et. al.³ have a good review of this. In general, the investigations show that removing mineral matter from coal decreases coal conversion, indicating that coal minerals are catalytically active in liquefaction. Canada Centre for Mineral and Energy Technology (CANMET) has reported lighter products from the two-stage coprocessing of coal and heavy oil with coal minerals compared to single-stage processing, at a given level of residuum conversion.⁷

Some of the previous work also attempt to determine what the catalytically active components in the mineral matter are. Iron sulfides (pyrites), magnetite, diaspore, and limonite have been reported as active components. Narain's (1987)³ review indicates that pyrite (FeS_2) and its decomposition products, such as pyrrhotite (Fe_{1-x}S , $0 < x < 1$), are the most active catalysts. A more detailed discussion of catalysis by pyrite will be presented in a later section. Table 2 lists other disposable catalysts, such as ores, ore concentrates,⁸⁻¹⁴ and wastes or residues from manufacturing processes¹⁵⁻²⁵ that have been investigated as liquefaction catalysts.

Ores and ore concentrates have also been investigated as disposable catalysts in coal liquefaction. Mathur, et. al. (1984)⁸ liquefied Pittsburgh seam (WV) bituminous in SRC-II heavy distillate using mixtures of pyrite with ores and ore concentrates containing minerals of potentially-active metals as slurry catalysts. Mixtures of pyrite and Ni limonite were more active than pyrite alone (of equivalent mass). FeS_2 + Mo oxide (small amounts), with or without Co oxide or hydroxide gave high yields of low-viscosity liquid. Ores containing Mo gave comparable oil yields, higher preasphaltene yields, and marginally lower asphaltene yields than commercial catalysts (e.g., Co-Mo/alumina.) In a subsequent

study, Mathur and Karri (1986)⁹ showed that a synthetic mixture of MoO_3 ore, limonite, and bauxite used for first stage liquefaction followed by liquefaction with $\text{Ni-Mo/Al}_2\text{O}_3$ gave results comparable to those using a commercial Co-Mo catalyst.

Manganese nodules which are naturally found on ocean and lake floors have been claimed as hydrogenation catalysts.^{10,11} When pretreated by leaching and/or sulfiding, they have also been claimed as hydrodesulfurization, hydrodemetallization, and hydrodenitrogenation catalysts for coal,¹² along with bog iron and nickel laterites.

Residues from various manufacturing processes that contain active metals have also been investigated as disposable catalysts. As previously mentioned, Bayer-Masse or red mud, a by-product of aluminum oxide processes, has also been used in coal hydrogenation. Veba Oel has numerous patents on red mud catalyst preparation and its use (with sulfur and/or with other oxides, such as Mn) in high pressure hydrogenation of coal and/or heavy oil.¹⁵⁻¹⁸ Catalytic activity has also been claimed for waste from production of lithopone, a pigment containing ZnS and BaSO_4 .^{19,20} Most of the patent claims cover 0.1-5.0 wt% addition of the disposable catalyst.²¹

Unfortunately, the low to medium activity of coal minerals and the other disposable catalysts requires more severe operating conditions than those used with supported catalysts. Sato, et. al. (1987)²⁶ liquefied Taiheyo coal at 440 & 450°C, 85 bar (1235 psi) initial pressure, and coal:tetralin of 1:3 using red mud and a catalyst prepared from gasification of coal liquefaction distillation bottoms. Although the latter gave higher oil yield, commercial NiMo and CoMo gave higher yields than both iron-based catalysts. Batenin and Lipovich (1991)¹⁴ investigated short-contact-time liquefaction of Kansk-Achinsk brown coal at 420-430°C using ore tailings, iron-based catalyst, and a Fe-Mo catalyst with 1% Fe (as $\text{Fe}_2(\text{SO}_4)_3$) and 0.2% Mo (as ammonia paramolybdate). Coal conversion improved with 0.5 wt% tailings. However, compared with the ore tailings, the Fe-Mo catalyst was less sensitive to donor solvent, especially at lower temperature. The inferiority of red mud compared to synthetic iron oxide and the beneficial

effect of Mo doping was also observed by Bacaud, et. al. (1990)²⁷ in their liquefaction of Freyming and Gardanne coals at 300-450°C and 150 bar H₂ (2180 psi) with 1-methylnaphthalene (1-MNP). Multicomponent catalysts will be discussed in greater detail in Section 3.4.

1.4 Catalyst activity

Catalyst activity is determined by the degree of dispersion and the morphology (form/phase/composition) of the catalyst. These factors are in turn affected by factors such as the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given coal and set of liquefaction conditions. Exactly how and to what extent they affect catalyst activity is not known. Moreover, most catalyst characterizations are reported for the catalyst either before or after the liquefaction. Obviously, the dispersion and morphology of the catalyst during liquefaction conditions are the determining factors.

1.4.1 Degree of dispersion

In most cases, the degree of catalyst dispersion is a qualitative description and is often inferred from the observed liquefaction performance. The ideal dispersed catalyst has a high surface area to volume ratio, intimate contact with, and uniform dispersion within the coal. Reucroft and Kim (1992)²⁸ performed an XPS study of various catalysts and catalysts impregnated onto coals. These included mixed oxides (such as Fe₂O₃/MoO₄⁻²), sulfated oxides (such as FeOOH/SO₄⁻², SnO₂/SO₄⁻², and FeOOH/SnO(OH)₂/SO₄⁻²) and promoted oxides (such as Mo/FeOOH/SO₄⁻² and Mo/Fe₂O₃/SO₄⁻²). For their catalysts, the analysis showed that the bulk concentration differed from the surface concentration; lower concentrations of both O and S were detected when going from the surface to the bulk. Dispersion methods (to be discussed in Section 2) attempt to increase the degree of dispersion.

The various studies which compare liquefaction using fine catalyst powders added to the coal with using impregnated catalyst precursors illustrate the greater coal-catalyst contact that can be attained with impregnation. Table 3 shows how impregnation can result in dramatic improvements in conversion to solubles for a bituminous coal compared to fine powder addition. However, this improvement may decrease as the powder size becomes small, e.g., sub-micron.

The impregnating solvent can also determine the level of dispersion. For example, organic solvents may be better able to penetrate the coal compared to water and so may produce better catalyst dispersion. The nature of the catalyst precursor is also important. For example, organometallic precursors may facilitate dispersion because they are miscible with the solvent which may be able to wet the coal better. The extent of wetting for the high-moisture low-rank coals may be different from that for the higher-rank coals. Moreover, there is the possibility of interaction between the precursor and the coal which can interfere with the transformation of the precursor into the catalyst active form. Buchanan, et. al. (1992)²⁹ have reported evidence for the possibility of solid-state interactions in dispersed catalysts. The activation conditions and the catalyst active form, in most cases, are unknown or not optimized. Catalyst dispersion methods will be discussed in greater detail in Section 2.

1.4.2 Catalyst active form/phase/composition

There are very few studies that attempt an in-situ characterization of the liquefaction catalyst. The catalysts are either characterized before or after liquefaction. Table 4a lists some studies on the characterization of active forms for catalysts, such as Sn, Mo, Ni, and Ru, based on analyses of the catalyst after liquefaction. Table 4b lists similar studies for Fe catalysts.

Since for most metals the sulfide is the most thermodynamically stable form under liquefaction conditions (if sulfur is present), it has

generally been regarded as the active form for metal compounds that have demonstrated catalytic activity. However, this may not always be the case depending on the coal, the presence of other metals, and the amount of sulfur present. For example, Rogers and Agnew (1981)³⁰ analyzed the inorganic constituents present before and after liquefaction of Morwell and Gelliondale (Australian) coals to determine the form of the catalytic components. They found that iron sulfides reduced to pyrrhotite, iron carboxylates to magnetite (Fe_3O_4), calcium carboxylates to vaterite (μCaCO_3), and tin oxide (precipitated onto the coal by hydrolysis of stannous chloride) to liquid tin, some of which reacted with H_2S to form herzenbergite (SnS). A later Japanese (1985) study of tin oxide as a dispersed fine particle catalyst found the oxide to be reduced to metallic tin, which was detected as small molten tin particles dispersed in the coal slurry under the liquefaction conditions studied.³¹ In a more recent study, Besson, et. al. (1990)³² investigated the liquefaction of French high-volatile bituminous Freyming coal at 350-430°C using various tin precursors (i.e., non-porous SnO_2 aerosol, presulfided SnO_2 , or commercial metallic tin). SnS was observed as the main product with small amounts of oxidized tin, although FeSn_2 was also observed in some cases. The active species was thought to be SnS , based on Mossbauer spectroscopy on the residues. In a study of ruthenium dispersed catalysts generated from organometallic complexes by Suzuki, et. al. (1992),³³ XPS analysis indicated the possibility of the existence of metallic Ru, in addition to the sulfide.

The iron sulfide system has been most studied (as seen from Table 4b) and the general consensus is that pyrrhotite, a non-stoichiometric sulfide, is the active form under liquefaction conditions. Section 5 presents a more detailed discussion of this. The studies for the iron sulfide system can be extended to other metal sulfide systems. Molybdenum sulfide has also been extensively studied, primarily in the petroleum refining field. It is generally recognized that MoS_2 is the active catalyst form with the edge planes as the active sites. However, recent studies³⁴ in coal liquefaction indicate that the active form may be a non-stoichiometric sulfide, as in the iron sulfide system. Mitchell, et. al. (1991)³⁴ formed MoS_2 from sulfided ammonium molybdate (SAM) as precursor. Even under

liquefaction with excess sulfur, the SAM was not fully converted to MoS_2 although the imperfectly sulfided precursor was more active. This may suggest a non-stoichiometric active form for the Mo sulfide, as for Fe. Section 4 presents a more detailed discussion of catalysis by molybdenum.

1.4.3 Catalyst activation and activity maintenance

The activation conditions vary with the catalyst precursor, as will be discussed with the various dispersion methods in Section 2. Ideally, these should be at conditions milder than or similar to liquefaction conditions. In the study of Mitchell, et. al. (1991)³⁴ with sulfided NH_4 molybdate (discussed in the previous section), the coal was liquefied under either H_2 or N_2 atmosphere with excess sulfur. Various temperature sequences were used: pretreatment (PT) to 275°F for 30 minutes; high-temperature treatment (HT) at 425°C for 30 minutes; or temperature-staged treatment (TS) combining PT and HT. Analyses of the catalyst residues after liquefaction did not show major differences in the catalysts, suggesting that the activation at 275°C may have been sufficient. Cugini, et. al. (1991)^{34a} found a similar optimum preactivation temperature of 275°C for Fe impregnated as FeOOH in the liquefaction of Illinois No. 6. An interesting finding in the Mitchell study is that the S/Mo under $\text{H}_2 < \text{S}/\text{Mo}$ under N_2 suggesting H was actively involved in the reduction of SAM (but not necessarily to MoS_2).

For disposable once-through catalysts, long-term activity maintenance may not be a concern. However, for catalysts based on expensive metals, such as Mo, catalyst recovery may need to be addressed. Recovery methods based on extraction³⁵⁻³⁸ have been claimed to be effective. For example, DOE has investigated the recovery of Mo from the coprocessing of model coal-ash/metal oxide mixtures,³⁹ Illinois No. 6, or deep-cleaned Kentucky with Maya atmospheric tower bottoms³⁵ using NH_4 molybdate at 435°C and 170 bar (2500 psig) for 2 hr. The THF-insolubles were ashed, then the ash was extracted with dilute aqueous NH_4OH at 65°C for one hr. A refractory Mo-V complex can be formed at high ashing temperatures; moreover, Ca molybdate

can be formed from Ca in the Illinois coal. A Mo recovery of >90% was obtained from cleaned coal from which most of Ca had been removed.

1.5 Overview of some DOE programs on dispersed catalysts

Work on process developments has essentially revolved around refinements to integrated two-stage liquefaction, which has been demonstrated on the pilot-scale at Wilsonville. Until recently, most of the Wilsonville work has been with supported catalysts (unimodal and bimodal Ni-Mo/alumina) all of which have proven effective. Recent work at Wilsonville has investigated liquefaction with combinations of dispersed Mo with supported catalyst; this will be discussed in a later section. PETC is currently focusing on dispersed catalysts and preliminary work has successfully achieved finely dispersed, highly-active Fe and Mo catalysts.⁴⁰ Several DOE-sponsored programs are involved in the development of similar catalysts using various synthesis and dispersion techniques, such as precipitation of nanoscale catalyst particles from microemulsions and production of catalysts using flame methods and laser pyrolysis, among others. The results from these investigations will be discussed in greater detail in various sections.

DOE has sponsored process development of UOP's coprocessing with dispersed catalyst since 1984. Gatsis at UOP has been developing coal liquefaction and coal/residuum coprocessing using a slurry catalyst. UOP's process patents⁴¹⁻⁴³ cover the use of finely divided dispersed metal catalyst -- selected from Groups IVB, VB, VIB, VIIB, and VIII. The precursor may be an oil-soluble or oil-insoluble compound (10 wppm to 4 wt% metal).⁴⁴ Specific catalyst preparations are claimed for V and Mo oxides (such as V_2O_5 and MoO_3) contacted with H_2S or NH_4S .⁴⁵⁻⁴⁸ The current effort is on the development of the Mo slurry catalyst. In this single-stage process, part of the liquid product from the high-pressure separator is recycled (5:1 recycle-to-fresh-feed ratio). For the coprocessing of Illinois No. 6 with Lloydminster resid (1:2 weight ratio, respectively), even at 0.05 wt% Mo, plant operability was good with no evidence of reactor fouling.⁴⁹ Temperatures as high as 465°C have been achieved with no reactor fouling

with 0.12 wt% Mo, an improvement over what was achieved with the previous V-based catalyst.⁵⁰ The improved high-temperature conversion and stability has been attributed to either or both of the more active Mo catalyst or/and the liquid recycle.⁵⁰ Moreover, catalyst recovery of >95% has been obtained on the bench-scale.⁵¹

2. CATALYST DISPERSION METHODS

This section discusses the methods for catalyst dispersion; the methods are classified according to the mode of introduction or addition of the catalyst. The broad classifications are: 1) catalysts introduced as fine powders; 2) catalysts generated in-situ from oil-soluble precursors; 3) catalysts generated in-situ from water-soluble precursors; and 4) catalysts introduced or generated via impregnation techniques. In the first class of methods, where the catalyst or catalyst precursor is mixed with the coal in the feed slurry, coal-catalyst contact may not be intimate. The other classes of methods attempt to increase this contact by incorporating the catalyst within the coal structure.

2.1 Finely-divided powders

The catalyst or precursor can be mixed with the coal/solvent slurry as a very fine powder which may be in the form of metals, oxides, oxyhydroxides, sulfides, oxysulfides, borides, carbides, nitrides, or phosphides, among others. In general, the contact achieved with dry mixing of the catalyst with coal is not as intimate as that achieved with the other dispersion techniques. However, if the powder particle size is small enough, the dispersion achieved may be satisfactory. The various methods discussed here deal with the production of the fine powder form of the catalyst; Table 5 lists these methods along with the catalyst forms that can be synthesized with the methods.

2.1.1 Precipitation methods for supported catalysts

The literature on preparation of supported catalysts reports on precipitation methods that form oxides or mixed oxides. If sulfides or oxysulfides⁵² are desired, they can then be generated by sulfidation. Nitrides,⁵³ borides, carbides, and phosphides can be generated in a similar manner, if they are the desired catalysts or precursors. Oyama (1992)⁵⁴ reviews the preparation and catalytic properties of transition

metal carbides and nitrides which have been evaluated for hydrodenitrogenation of coal-derived liquids, among others.

Sulfides can also be directly prepared using a non-aqueous precipitation method wherein a metal chloride is dissolved in ethyl acetate followed by addition to a slurry of Li_2S to precipitate the metal sulfide.⁵⁵

Precipitation methods used for supported catalyst preparation, in general, involve the precipitation of a metal salt on to an oxide support surface by varying the pH of the solution heterogeneously or homogeneously, e.g., by dropwise addition of the precipitating agent.⁵⁶ The catalyst fine powder may be obtained by detachment from the support.⁵⁷ The following are some precipitation methods (the descriptions are generalized for multicomponent systems):⁵⁸

- 1) Gel precipitation: organic gelling agent is added to aqueous metal salt solution before precipitation; for a bimetallic system, contact with an alkali precipitant (e.g., NH_4OH) results in formation of a co-precipitate such that the metallic hydroxide is held rigidly within the framework of the organic gel
- 2) Sol-gel formation: colloidal solution of metallic oxide(s) or hydroxide(s) is converted to a semi-rigid gel by a number of mechanisms, such as removal of water, neutralization with base, or removal of acid by solvent extraction. The gel is then dried and calcined to the oxide.
- 3) Aerogel formation: Mixed aerogel is prepared by addition of small amount of water to a solution containing the dissolved metal compound(s). The solvent is then stripped under supercritical conditions.
- 4) Homogeneous pH control: the precipitant (OH^-) is generated homogeneously throughout a suspension in a solution of the active metal by thermal or chemical decomposition of urea.

-- For example, catalyst prepared by mixing urea with FeSO_4 has been claimed to result in less gas make during conventional coal liquefaction conditions.⁵⁹

2.1.2 Microemulsion-based synthesis techniques

There is a growing interest in production of very fine catalyst particles using microemulsion-based synthesis techniques. Matijevic (1988)⁶⁰ reviews the principles involved in the formation of colloidal dispersions of metal oxides, carbonates, sulfides, selenides, phosphates, titanates, and ferrites by precipitation from homogeneous solutions. Microemulsions have also been used to prepare monodisperse colloidal transition metal particles⁶¹⁻⁶⁴ and alloy powders^{65,66}. Although most of the applications have been in ceramics,⁶⁷ the synthesis methods have been increasingly used to produce catalysts for Fischer-Tropsch synthesis^{68,69} and coal liquefaction. Work at Sandia National Laboratories has looked at colloidal titanates as potential coal liquefaction catalysts.^{70,71} For example, Snape, et. al. (1988)⁷¹ have investigated the hydrolysis of a bituminous coal at 500°C and 152 bar (2205 psi) H_2 with various catalysts, including a titanate. The tar yields achieved were 26% with no catalyst, 36% with ZnCl_2 , 54% with SnCl_2 , 59% with MoS_2 , and 64% with 0.7% Pd on hydrous TiO_2 .

Various DOE-sponsored programs at Sandia,^{72,73} Batelle,⁷⁴ and West Virginia University⁷⁵ are investigating the production of iron-based liquefaction catalysts using emulsion techniques. Linehan, et. al. (1992)⁷⁴ prepare nanometer-sized iron oxide catalysts from reverse micelles by rapid thermal decomposition of soluble precursors such as $\text{FeNH}_4(\text{SO}_4)_2$. The catalysts prove to be good, selective catalysts for C-C bond scission.

Pennsylvania State University is synthesizing molybdenum sulfide particles in microemulsions by adding ammonium molybdate to sulfuric acid-solubilized microemulsions containing a non-ionic surfactant. By varying the water to surfactant mole ratio, catalyst particle size and surface area can be varied.⁷⁶ Liquefaction of Wyodak coal at 350°C with 100 ppm

Mo of this catalyst has resulted in a yield of 80% hexane-solubles, which was equal to or greater than those obtained from impregnation with ammonium molybdate.⁷⁷

An attractive advantage of the microemulsion route to dispersed catalyst is the production of very fine (up to nanosized) particles with a narrow size distribution. The effects of the surfactants used in the emulsions on liquefaction behavior may be adverse. However, microemulsions can be prepared without surfactants, e.g., from hexane, water, and isopropanol.⁷⁸

2.1.3 Deposition via surface wetting

Incipient wetness techniques as developed for supported catalysts have been used to deposit the catalyst or precursor onto coal, which acts as the support for the dispersed catalyst. In the standard method, a strongly bridging solvent, such as water, is used to dissolve the metal salt precursor. Then the mixture is added dropwise to the coal until the coal is at "incipient wetness", i.e., the point where unbound moisture is about to become available.⁵⁸

There are other techniques that are referred to as incipient wetness methods that are variants of the above. In some of these, the support (or coal) is first impregnated with an organic liquid until only a thin surface element of the coal is left dry. Then, the coal is impregnated with an aqueous solution of the metal salt to give a surface-coated coal particle. The coal particles are subsequently dried. In yet another variation, the coal is first slurried with a water-immiscible liquid before the aqueous impregnating solution is added to displace the water-immiscible liquid from the pores of the coal.

Obviously, the variety in the methods results in differences in properties of the catalysts generated. For example, Milburn, et. al. (1989)⁷⁹ looked at the effects of solvent and method of solvent removal for alumina-supported liquefaction catalysts. The use of a less polar solvent and

subsequent rapid removal of the solvent minimized compaction of the colloidal alumina particles.

For multicomponent catalysts, e.g., bimetallic systems, the general procedure is to use one reactant as a high-surface area template (e.g., Mg). This is then reacted with the other metal carrier, e.g., ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), to form the surface compound. The excess template is removed by solubilization techniques (e.g., remove excess MgO with dilute HCl; the dried product is $\text{Mg}_2\text{Mo}_3\text{O}_8$).⁵⁸

2.1.4 Other methods

Flame decomposition is usually used to form metals. In this method, the vapor of a metal salt, such as metal chloride, is directed into the flame of an $\text{O}_2\text{-H}_2$ burner, followed by reduction by H_2 of the product to convert the oxide to the metal. The H_2 reduction may be replaced by a sulfidation to form the sulfide.⁵⁸ Fe_2O_3 and SnO_2 (10-200 nm) aerosols prepared from such a flame method were used in the liquefaction of Freyming coal, a French high-volatile bituminous coal.^{32,80,81} These flame processes, used primarily in the production of ceramic powders like the microemulsion-based techniques, also have the potential to produce nanometer-sized particles.⁸²

Radiation chemistry techniques have also been used to produce fine metal particles. Argonne Laboratory has been investigating the evolution of chalcogenide particles by laser photolysis that allow good control of particle size.⁸³ Ongoing work at University of Kentucky is on the production of nanometer-sized iron-based catalysts using a CO_2 laser pyrolysis system.^{84,85} Spherical 3-13 nm orthorhombic Fe_3C and metastable hexagonal Fe_7C_3 were prepared by laser pyrolysis of gas mixtures of $\text{Fe}(\text{CO})_5$ and ethylene. After in-situ sulfidation with dimethyldisulfide, these carbides were tested and compared with metal sulfides prepared from $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{C}_5\text{O}_2\text{H}_7)_3$, and Mo naphthenate in the liquefaction of Western Kentucky No. 6 bituminous and Wyodak subbituminous at 405°C and 55 bar

(800 psi) H_2 (cold) for 15 minutes. All catalysts enhanced coal conversion over thermal or non-catalytic liquefaction.

Both spray drying and freeze drying of an aqueous metal salt solution with subsequent H_2 or chemical reduction of the salts can be used to produce finely-dispersed powders.

2.1.5 Relative activities of powdered catalysts

There have been numerous studies comparing the activities of various fine powder catalysts or catalyst precursors for a given reaction and set of conditions. For example, Tarrer, et. al. (1988)⁸⁶ compared the hydrodenitrogenation (HDN) performance of the precipitated transition metal sulfides Cr_2S_3 , MoS_2 , WS_2 , RuS_2 , FeS_x . The sulfides, prepared using a non-aqueous precipitation method,⁵⁵ had surface areas of 5-80 m^2/g . Activity and selectivity of these sulfides were evaluated using both a quinoline model compound system (380°C, 30 min.) and Kentucky #1 coal (400°C, 60 minutes) at 1250 psi (cold) H_2 . RuS_2 was the most active in terms of quinoline hydrogenation. The precipitated catalysts were more active than commercial $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, except for FeS_x . For HDN of quinoline, the most active were $NiMo/Al_2O_3$ and RuS_2 which showed similar HDN activities; precipitated catalysts had coal HDN activity but $NiMo/Al_2O_3$ was more active.

Tekely, et. al. (1988)⁸⁷ liquefied French Freyming coal for one hr at 140 bar H_2 (2030 psi) using sulfided Fe, Mo, and Sn aerosols produced from the combustion of metal chloride vapors. At 2 wt% catalyst on coal loading, the catalysts accelerated hydrogenolysis of bridging bonds (especially ether bonds) and hydrogenation of polyaromatic units, with the relative activities being $Fe_2O_3 \sim MoO_3 \gg SnO_2$.

2.2 Oil-soluble precursors

Sections 2.2 and 2.3 discuss oil- and water-soluble catalyst precursors, respectively. Tables 6a and 6b lists various oil- and water-soluble precursors (respectively) that have been studied or claimed for coal liquefaction. The table includes precursors that have been used with pretreatments (to be discussed in Section 2.4.2).

Oil-soluble catalysts and precursors can be mixed in with the coal/solvent slurry. Most of the precursors that have been used are organometallics. As homogeneous catalysts, organometallic compounds may maximize contacting with coal. They can be highly active, specific, and selective; they may also be more poison-resistant than heterogeneous systems. Advances in the synthesis of polynuclear cluster complexes (e.g., Pt and Ir, Au and Rh) and the ability to anchor such complexes to heterogeneous surfaces have been used. In the latter case, there is a possibility of complex cross-linking, though.

In general, oil-soluble and water-soluble precursors (to be discussed in Section 2.3) give liquefaction performance better than thermal liquefaction. For example, Hirschon and Wilson (1989)⁸⁸ found that the use of either aqueous salts or organometallic complexes of Mo gave superior conversions over thermal liquefaction with Illinois No. 6 in tetralin at 34 bar (500 psi) H₂ (cold) and 400°C. The best organometallic precursor was a dimeric molybdenum sulfido complex that did not require high-temperature activation.

The catalyst effectiveness can also be a function of coal type and the catalyst precursor. In a subsequent SRI study, Hirschon and Wilson (1992)⁸⁹ found that Fe catalyst precursors were not effective for Illinois No. 6; however, Fe catalysts were effective for Beulah Zap ND lignite. Moreover, catalysts from organometallic precursors gave higher yields of toluene-solubles than catalysts from water-soluble salts or than reaction without catalyst. Yields with organometallic precursors were as high as those in tetralin with no catalyst, indicating that donor solvents may be unnecessary with a good catalyst precursor. In a microscopic study of Fe

and Mo liquefaction catalysts by Mitchell et. al. (1991)³⁴, he found that Mo generated from sulfided NH_4 molybdate was associated with the organic phase unlike Fe from FeSO_4 which was in agglomerates. This may explain why Mo was more effective than Fe. However, there was also indication from energy dispersive analysis of the catalyst residues that the Mo was only dispersed on the surface and did not penetrate throughout the coal particle. Moreover, the Mo catalyst coating "peeled" from the coal surface with reaction time.

2.2.1 Naphthenates and octoates

Naphthenates and octoates are among the most studied organometallic catalyst precursors for coal liquefaction. Curtis et. al. (1988)⁹⁰ tested Mo naphthenate, Amocat 1B, and precipitated MoS_2 with model compounds at a concentration of 1 or 2 wt% in hexadecane solvent, 380°C, and 87 bar (1250 psi) H_2 (cold). While all three catalysts had the same hydrodesulfurization (HDS) activities and were ineffective for hydrocracking, Mo naphthenate was most effective for hydrogenation, hydrodeoxygenation (HDO), and HDN. In the liquefaction of Illinois No. 6 in anthracene at 425°C, 1250 psi H_2 (cold), Mo naphthenate was most effective for coal conversion, HC production, production of $\text{MeCl}_2/\text{MeOH}$ -soluble material, HDN, and HDO.

The relative activities of Mo, Ni, and V organometallic complexes have also been investigated in Auburn University studies by Kim, et. al. (1990).⁹¹ Oil-phase naphthenates or octoates, and solid-phase acetylacetonates were used in the coprocessing of Illinois No. 6 with Khafji or Maya resid at 400°C, 195 bar (2820 psi) H_2 and 425°C, 208 bar (3000 psi) H_2 . The relative activities were in the order $\text{Mo} \sim \text{Ni} > \text{Ni-Mo}/\text{Al}_2\text{O}_3 > \text{S(thermal)} > \text{V}$.

Kim, et. al. (1991)⁹² further investigated the effectiveness of Ni in the hydrogenation of the model systems naphthalene, indan and indene, benzothiophene, o-cresol and benzofuran, or quinoline and indole in hexadecane solvent. The catalysts were generated from Ni naphthenate,

octoate, acetylacetonate, or citrate. At a level of 2900 ppm Ni, all precursors except for naphthenate were active for hydrogenation and the relative activities were in the order acetylacetonate > citrate > octoate.

In an Exxon patent, it is claimed that mixing 0.1-2 wt% of an oil-soluble Cr compound, such as naphthenate, with a hydrocarbon oil and heating the mixture with an H₂S-containing gas in the absence of coal, produces a catalyst precursor that when added to the coal/solvent slurry, results in good liquefaction performance at 425-480°C and 29-345 bar (400-5000 psi) H₂.¹¹⁶

2.2.2 Carbonyls

Fe and Mo carbonyls have been among the most studied carbonyls. A 1983 Japanese patent⁹³ claims that Fe(CO)₅ with free or coal sulfur converts to a high-activity catalyst for coal liquefaction at about 300°C. Watanabe, et. al. (1984)⁹⁴ liquefied Japanese Mi-ike bituminous and Taiheiyō subbituminous coals at 445°C with Fe(CO)₅, [Fe(CO)₂Cp]₂ (Cp=cyclopentadienyl), ground red mud, FeCl₃, FeSO₄, and Fe(III) acetylacetonate. In general, the presence of these Fe compounds resulted in increases in the lighter fractions (oil and asphaltenes) but Fe(CO)₅ showed the highest activity. [Fe(CO)₂Cp]₂ did not show high activity probably because higher temperatures (>445°C) are required to form the active species.

Herrick, et. al. (1990)⁹⁵ used Fe(CO)₅ in the coprocessing of Illinois No. 6 with Maya atmospheric residue. The use of 0.5 wt% Fe as Fe(CO)₅ increased coal conversion to MeCl₂-solubles from 39% to 82%. 95% of the Fe in the Fe(CO)₅ precursor decomposed to a mixture of highly-dispersed pyrrhotite with a 12 nm mean crystallite size. The remainder of the Fe decomposed to Fe₃C and other iron compounds.

In addition to Fe(CO)₅, Pennsylvania State University researchers have also done work with Mo(CO)₆ and mixtures of Fe(CO)₅ and Mo(CO)₆. In general, the order of catalyst activities is Fe(CO)₅/Mo(CO)₆ > Mo(CO)₆ >

Fe(CO)₅ with respect to yield of pentane-soluble products.^{96,97} This work by Pradhan, et. al. on carbonyls will be discussed in greater detail in Section 3.3 as their performance relate to that of sulfated oxides.

Suzuki, et. al. (1992)³³ studied Ru-based catalysts generated from the following precursors: Ru (cyclooctadiene) (cyclooctatriene), Ru (acetylacetonate)₃, and Ru₃(CO)₁₂. Liquefaction with 1-MNP at 400-425°C and 55 bar (800 psi) H₂ (cold) were conducted with Australian Yallourn brown coal, Wyoming, Illinois No. 6, and Mi-ike Japanese bituminous coals. All coals were liquefied with high conversion with only small amounts of the Ru complexes (0.02-0.07%). Ru complexes were found to be more effective in promoting preasphaltene to asphaltene and asphaltene to oil conversions compared to Fe(CO)₅-S. Ru₃(CO)₁₂, when used as a promoter for supported CoMo, was also found to be effective as an active amine transalkylating catalysts for hydrogenolysis reactions of C-N bonds based on reactions with the model compound tetrahydroquinoline by Hirschon, et. al. (1988).⁹⁸

Warzinski, et. al. (1992)⁹⁹ at DOE investigated an alternative method of impregnating Mo(CO)₆ into coal. The method utilizes supercritical CO₂; the solubility and phase behavior of the carbonyl in supercritical CO₂ at 40, 50, and 60°C have been reported and preliminary liquefaction results with Illinois No. 6 impregnated by this method suggest that coal dissolution is promoted.

2.2.3 Molybdic and phosphomolybdic acids

Molybdic acid (H₂MoO₄) in combination with other compounds, such as ZnO+magnesia or chromic acid, was found to be effective in liquefaction by the early German work. Exxon has several patents on various formulations containing molybdic acid¹⁰⁰ and phosphomolybdic acid H₇[P(Mo₂O₇)₆]¹⁰¹⁻¹⁰⁴ for the hydroconversion of carbonaceous material. The latter has been claimed to have higher activity and better coke control.¹⁰¹ On a Mo basis, sulfided molybdic acid at a 0.2-2 wt% Mo on oil loading is claimed to be 57% more active than Mo naphthenate.¹⁰⁰

Bearden and Aldridge of Exxon patented catalysts that contain phosphomolybdic acid for the hydroconversion of coal, oil, and coal/oil mixtures. In the parent patent, 10-950 ppm Mo (preferred are phosphomolybdic acid and Mo naphthenate) is used as catalyst in the coprocessing of 2-50% coal at 375-415°C.¹⁰⁴ In a second patent, the catalyst consists of 1-2000 ppm of Mo (especially phosphomolybdic acid and Mo naphthenate) with 0.1-20 moles/g-atom metal of a hydrogen halide. In the hydroconversion of coal or oil at 315-455°C and 35-345 bar (500-5000 psi) H₂, the halide is claimed to improve metals removal, Conradson carbon conversion, and coke suppression.¹⁰³ In these patents, H₂S is added to produce the active catalyst. In a later Exxon patent by Lewis and Mayer (1987)¹⁰⁵, the catalyst precursor preparation did not require the addition of H₂S. 0.2-2 parts weight Mo as phosphomolybdic acid was mixed with 100 parts weight of the oil prior to contacting with a H₂-containing gas at 40-370°C to remove the water. A portion of the resulting mixture is then mixed with the oil then reheated in a 370-565°C H₂-containing gas.

2.2.4 Others

Commercial oil-soluble Mo-based additives, such as Molyvan L or Molyvan 322, have been used to liquefy Illinois No. 6¹⁰⁶ and Black Thunder subbituminous¹⁰⁷ coals. These additives, which already have Mo-S bonds, have an advantage in that no sulfiding is required. Results with these relatively new catalysts will be discussed in greater detail in Section 4.4.

Tetraethyl lead has also been investigated as a catalyst precursor with bituminous Australian, mostly Millmeran, coal.¹⁰⁸ It improved conversions although yields were not as high as those from iodomethane as catalyst; lead acetate or tetramethyl tin also gave reasonable oil yields.

Cobalt-based catalysts have also been investigated for coal liquefaction. Wilson, et. al. (1988)¹⁰⁹ liquefied Illinois No. 6 (River King) with SRC-II recycle solvent at 425°C for 15 min. using bis(dihydrobis(pyrazolyl)borate)cobalt(II), an oil-soluble organometallic

salt. At 0.2 wt% Co loading, coal conversion (based on daf coal) and conversions to cyclohexane- and THF-soluble products at 2010 psig were about the same as those obtained with the water-soluble precursor NH_4 molybdate at 1.6 wt% Mo and 125 bar (1800 psi) H_2 . With water-soluble cobalt(II) sulfate heptahydrate as precursor, conversions were only slightly better than in the absence of catalyst.

Another cobalt-based catalyst that has been studied is Co phthalocyanine (Co-PhCy). Sakamoto, et. al. (1989)¹¹⁰ obtained a liquid yield of 4% without catalyst and 15% with catalyst for liquefaction at 380°C and 100 bar (1450 psi) H_2 (cold). They claim that the Co-PhCy catalyst held a lot of H_2 and promoted the decomposition of asphaltene by donating H_2 to the radicals produced during hydrocracking.

A Japan Synthetic Rubber patent¹¹⁵ outlines the synthesis of a thiolate, $\text{Mo}(\text{t-C}_4\text{H}_9\text{S})_4$, a dark red crystalline solid unstable to moisture and air, which may be used to synthesize other Mo complexes that can be used as soluble catalysts.

Organic sulfur compounds have also been claimed as effective catalysts. Charcosset, et. al. (1986)¹¹¹ have used benzenethiol as soluble catalyst for coal liquefaction. Rudnick has European patents on the use of thiol, thiophenol, benzothiophene, and 2- to 12-carbon alkyl mercaptans as hydrogen transfer agents.^{112,113} A French patent¹¹⁴ claims that an oil-soluble ferric complex of at least one sulfonic acid and containing 6-12 g-atoms Fe per g-equiv of acid can be effective for liquefaction with donor solvent at 400-470°C, and 60-250 bar (870-3630 psi). For example, for a catalyst prepared from $\text{Fe}(\text{OH})_3$ and a 10- to 35-carbon alkylbenzene sulfonic acid, higher conversions (84-86%) and distillate yields compared to no catalyst or to FeCl_2 are obtained.

The use of colloidal metals as fine powder catalysts was mentioned in a previous section. In a study by Bonnemann, et. al. (1992)⁶¹, nanometer colloidal metals were produced by the reduction of the metal salts with hydrotriorganoborates. The quaternary ammonium halides that were formed coated the colloidal particles and provided solubility in organic solvents

and high stability. It was reported that hydrogenation catalysts made by this method had twice the activity of standard catalysts. It is possible then to alter the solubility of the metal catalyst precursor by this selective halide coating.

2.3 Water-soluble precursors

These precursors can be introduced onto the coal by any of the surface wetting deposition methods discussed in Section 2.1.2.

2.3.1 Molybdates

Various molybdates, particularly ammonium molybdates, have been investigated as catalyst precursors. Li, et. al. (1991)¹¹⁷ have found that with 0.5% Mo added as ammonium tetrathiomolybdate, NH_4MoS_4 (ATM), higher yields of oil and phenols, and lower sulfur in oil compared to the non-catalytic case were attained. Burgess, et. al. (1991)¹¹⁸ have used sulfided ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$ (AM), sulfided tetrahydroquinolinium molybdate, and ATM as MoS_2 precursors with five coals using naphthalene or phenanthrene as solvents. Their results with bituminous coals indicate that Mo provided atomic H to help crack asphaltenes to oils. In the investigation of Davis, et. al. (1991)¹¹⁹ of ATM as precursor, H_2 or N_2 atmosphere was used in the liquefaction of lignite, subbituminous, high-volatile C, and high-volatile A coals. As in the Burgess, et. al. study,¹¹⁸ the catalyst minimized retrogressive reactions in the subbituminous coal. H_2 and catalyst promoted liquid conversion and the thermoplastic development of vitrinite, due to enhanced H transfer and catalyst dispersion.

This catalyst enhancement of conversion was also demonstrated by Derbyshire, et. al. (1988)¹²⁰ in the liquefaction of PSOC-1403P subbituminous coal with no donor solvent using ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (AHM). The results suggest that the catalyst provides a source of H atoms by dissociating molecular hydrogen and that the H atoms induce cleavage of bridging linkages and stabilize the resulting

fragments. Garcia and Schobert (1989)¹²¹ studied the liquefaction of a high-sulfur (12% S) lignite with no solvent using ATM, sulfided AHM, and MoS_2 as catalysts. The best conversions, liquid yields, and HDS were obtained with the impregnated sulfided AHM at 325°C. At temperatures <325°C, the other precursors did not decompose to the active catalyst form.

The catalyst activation temperature is also a function of the form of the catalyst precursor. Bockrath, et. al. (1992)¹²² mixed Illinois No. 6 coal with 40% of its weight of an aqueous solution of AHM or ATM followed by vacuum drying at 60°C. In another case, AHM was added as a powder. During liquefaction at 350°C, the AHM powder performed only marginally better than coal without added catalyst even though twice as much Mo was added in the powder form. At this low temperature liquefaction, it is important that the catalyst be in its active form. Utz, et. al. (1990)¹²³ liquefied Illinois No. 6 with tetralin (1:2 coal:solvent) at 425°C and 70 bar (1000 psi) H_2 (cold) for one hr using 1000 ppm Mo on coal. At these conditions, the catalyst precursors (aqueous AHM, ATM, aqueous suspension of MoS_3 , and dry MoS_3) were sufficiently activated.

The impregnation solvent can also have an effect on the catalyst effectiveness. Huang, et. al. (1992)¹²⁴ liquefied Montana subbituminous using ATM as catalyst precursor dispersed by an incipient wetness method. Water and a mixture of water/THF were employed as impregnation solvents. The volume of water/THF required to achieve incipient wetness was thrice that of pure water so that better liquefaction (probably due to better catalyst dispersion) was achieved with coal impregnated using water/THF.

2.3.2 Sulfates

As mentioned in the early history of coal liquefaction, ferrous sulfates were used as slurry catalysts in the liquefaction of brown coals. In a recent study, Yokohama, et. al. (1989)¹²⁵ used diphenylether and diphenylmethane to study the activities of FeS_2 , $\text{Fe}_2\text{O}_3 + \text{S}$, $\text{Fe}_3\text{O}_4 + \text{S}$, red mud (contg. 40% Fe_2O_3) + S, and FeSO_4 at 101 bar (1465 psi) H_2 or N_2 (cold)

and 450°C. The sulfate always formed in the presence of water (but never without it) and promoted formation of radicals from phenyl and benzyl groups by dehydrogenation; these radicals polymerized to less volatile compounds under both N₂ and H₂.

Ammonium sulfate has also been tested by Yokohama, et al. (1991)¹²⁶ for the liquefaction of a pyrite-containing Japanese bituminous coal and a pyrite-free Australian lignite; however, it did not demonstrate any activity for coal hydrogenation with tetralin at the same conditions stated previously. Moreover, there was a difference in the products from liquefaction of Japanese bituminous with (NH₄)₂SO₄ compared with that from FeS₂. The coal liquids from FeS₂ consisted of aromatics with short side chains and fewer heteroatoms whereas with (NH₄)₂SO₄, the side chains were longer and had more heteroatoms.¹²⁵

The use of sulfated metal (particularly iron) oxides as coal liquefaction catalysts with excellent hydrogenation and hydrocracking activities has been researched extensively by groups at University of Pittsburgh and in Japan. This work will be discussed in greater detail in Section 3.3.2.

2.3.3 Others

In a study by McCandless, et. al. (1981),¹²⁷ metal chloride was impregnated at 3 wt% on pulverized Montana Rosebud subbituminous coal which was then liquefied at 450°C, 69 bar (1000 psi) H₂ with 5% HCl/H₂. The alkaline earth metal (Ca, Sr, Ba, Ra) chlorides had some catalytic effect, but the alkali metal (Group IA) chlorides seemed to act as poisons. The relative reactivities were in the order FeCl₂ < ZnCl₂ < NiCl₂ < CuCl₂ < SnCl₂ < CoCl₂. Nonvolatile chlorides remained in the unreacted residue in chloride form but they could be easily removed by water leaching. Exxon has several patents on the use of one or more iron or zinc chlorides¹²⁸ and hydrogen halides^{103,129} for the hydroconversion of coal and oil.

Takemura and Saito (1984)¹³⁰ found that Ni acetate was effective for coal conversion in the liquefaction of Morwell brown coal with phenolics as solvent at relatively low temperatures of 230-270°C. XRD analysis of the catalysts after runs showed the presence of metallic Ni, indicating that Ni acetate converted to acetic acid and Ni. Ihara (1985)¹³¹ claims a similar advantage with the use of phenol and/or alkylphenol; a partially hydrogenated product with good H-donor properties can be produced with one or more Group VI and/or VIII metal sulfides.

Exxon has numerous patents on other water-soluble catalysts for hydroconversion of coal and/or oil, such as aqueous solutions of oxalates of V and Mo³⁷ and aqueous solutions of CrO₃ to which a water-soluble compound such as an alcohol or carbohydrate has been added.¹³²⁻¹³⁴ In the case of t-butanol added to CrO₃, it has been claimed that hydroconversion performance for a vacuum residue was comparable to that obtained with Cr naphthenate.¹³² In another Exxon patent, the salt of a metal-sulfur analog of cubane or a mixture of such analogs mixed with solid HC feed, and an ammonium and/or hydrocarbyl substituted ammonium has been claimed to be effective in the hydroconversion of solid carbonaceous materials. The metal-sulfur cubane analog is converted to the sulfide during hydroconversion at 260-480°C and 35-483 bar (500-7000 psig) H₂ and is claimed to be highly dispersed and gives high conversion.¹³⁵

2.4 Impregnation techniques

In the deposition by surface wetting methods discussed in Section 2.1.3, both the metal salt and its counter ion are deposited on to the support (i.e., coal for dispersed catalysts). The metal salt is then dispersed by diffusion through the liquid-filled pores, or by capillarity if the support is dry. These methods are usually used when there is little interaction between the metal salt and the support, which just acts as a solid surface.⁵⁶ In the impregnation techniques discussed in this section, there may be an interaction between the deposited catalyst precursor and the coal support.

2.4.1 Ion-exchange

Ion exchange takes advantage of ion adsorption properties to prepare catalysts in solution from metal salts. Unlike deposition by surface wetting, only the adsorption of a given type of ions occurs; none of the corresponding counterions are adsorbed. If the surface charge and charge density are properly selected by appropriate pH control, it may be possible to have dispersion of the metal ion at the atomic level. The pH of the metal salt solution can be viewed to act as a "surface charge selection switch".⁵⁶

The ability to introduce metals by ion-exchange is particularly promising with low-rank coals which contain ion-exchangeable functional groups like carboxyls. These carboxyl groups can occur either as carboxylic acids or as groups associated with cations such as Ca, Mg, Na, and Fe. For example, Fe has been successfully ion-exchanged into Taiheyo Japanese subbituminous coal^{136,137} and Morwell brown coal,¹³⁶ among others. In the latter case, ion-exchange with ferrous sulfate or acetate resulted in a catalyst that had higher activity than Fe_2O_3 powders mixed with the coal.¹³⁸ It has also been found that coal conversion was unaffected by changing the counter anion (e.g., sulfate, chloride, or acetate) of the treatment solution.¹³⁹

2.4.2 Pretreatment combined with soluble precursors

In general, incipient wetness, impregnation, and soluble precursor techniques produce catalysts that are more effective than precipitated fine powders that are mixed with the coal. For example, in a study of various molybdenum-based catalysts, Mo naphthenate was more active than a precipitated poorly crystalline MoS_2 .¹⁴⁰ A possible exception may be ultrafine, nanosized powders precipitated via microemulsion techniques which may result in good dispersion that can be comparable to that obtained by the other techniques. For example, the 3-13 nm iron carbide precursors synthesized at University of Kentucky enhanced conversion of

Wyodak in tetralin at 385°C, 55 bar (800 psi) H₂ (cold) to a greater extent than that obtained with Fe(CO)₅ precursor.¹⁴¹

Solvent swelling of coal combined with catalyst impregnation followed by liquefaction can result in enhanced conversions and yields. Artok, et. al. (1992)¹⁴² swelled Blind Canyon high-volatile bituminous and Big Brown lignite with methanol, pyridine, tetrahydrofuran (THF), or 10% t-butyl ammonium hydroxide (TBAH) in aqueous 50% methanol. Swollen and unswollen coals were impregnated with NH₄ tetrathiomolybdate and MoS₃, then liquefied in phenanthrene at 275°C and 69 bar (1000 psi) H₂. Without swelling, the catalysts increased conversion mainly due to increased yield of preasphaltenes; without catalyst, swelling improved conversion mainly due to higher yield of oil + gas. For bituminous coals, preswelling with methanol or pyridine had little effect but THF and TBAH enhanced conversion. Pre-swollen coals impregnated with ferrous sulfate, Mo(CO)₆, and Fe(CO)₅ gave better liquefaction behavior than the unswollen coals.¹⁴³ In ion-exchanging Taiheyo Japanese subbituminous coal using aqueous FeSO₄ solution, Miki, et. al. (1991)^{136,137} also added ethanol to improve coal swelling. In another Japanese study,¹⁴⁴ Morwell Australian brown coal was impregnated with ZnCl₂ or SnCl₂ from a methanol solution, followed by sulfidation of the metal chloride with 5% H₂S at room temperature. Flash pyrolysis of the swollen/impregnated coal resulted in increased coal conversion and oil yields.

Prehydrogenation of swollen impregnated coals at mild H₂ pressure and ambient temperature followed by liquefaction is one embodiment of a patent by Joseph (1991).¹⁴⁵ Bolton and Derbyshire (1988)¹⁴⁶ prehydrogenated Linby high-volatile bituminous coal that had been impregnated with 1 wt% Mo from aqueous NH₄ tetrathiomolybdate. Compared to the unhydrogenated coal, the treated coal resulted in increases in overall conversion and liquid yield during pyrolysis; hydrolysis increased these even more. In hydrolysis, the same conversion was achieved using catalyst-impregnated but unhydrogenated coal, indicating that reactions occurring in catalytic hydrogenation and early in hydrolysis may be the same. In a subsequent study, Derbyshire, et. al. (1990)¹⁴⁷ impregnated a lignite and two bituminous coals with Mo, Fe, or Fe/Mo prior to prehydrogenation

at 7 MPa H₂ and 275°C for 30 minutes. For liquefaction at 425°C and 30 minutes, the performance of the Mo and Fe/Mo catalysts were comparable and superior to Fe. Increasing coal rank decreased oil yield, oil/asphaltene ratio, and CO_x yield.

Baldwin and Miller (1990)¹⁴⁸ combined mild alkylation and addition of a dispersed catalyst (chlorine) via HCl as alkylation catalyst. The presence of the dispersed catalyst was more effective than alkylation in terms of net reactivity enhancement.

The effectiveness of organic reductions with sodium or potassium as pretreatments was investigated by Nomura, et. al. (1985).¹⁴⁹ Taiheyo coal impregnated with FeBr₂ was co-reduced with either Na in NH₃ or with K in refluxing THF prior to liquefaction with tetralin. Non-catalytic (no Fe) liquefaction of pretreated coals resulted in higher hexane solubles yields than those obtained without the pretreatment. Fe increased benzene- and hexane-solubles compared to non-catalytic liquefaction of K-treated coal. The slight increase of H atoms added to coal and the loosening of clusters of aromatic sheets was a possible explanation.

Ha, et. al. (1988)¹⁵⁰ deposited either a water-soluble Fe or Mo catalyst onto coal particles before or after agglomeration with SRC-II heavy distillate at 0.35:1 to form 2-3 mm diameter agglomerates which were then reacted at 400°C and 91 bar (1300 psig) H₂ (cold). When the catalyst was Fe (+H₂S addition), higher THF-solubles yield resulted when impregnation was prior to agglomeration. However, the reverse was true with Mo. It is possible that some of the Fe may have been removed by the H₂O during the agglomeration step. A patent has been issued on this agglomeration of catalyst-impregnated coals.¹⁵¹

The use of ultrasound to enhance catalyst dispersion during coal liquefaction has been investigated by Bendale, et. al. (1991).¹⁵² Two-stage liquefaction experiments have been conducted with Mo naphthenate or Mo carbonyl as catalyst precursors along with stoichiometric amounts of elemental sulfur.

3. DEVELOPMENTS IN DISPERSED CATALYSTS

This section provides a general review of relevant developments in dispersed catalysts for petroleum hydroprocessing and coal liquids upgrading, and fundamental research in the areas of effect of sulfur during liquefaction, sulfated oxide ("superacid") catalysts, and multicomponent catalysis.

3.1 Applications in petroleum hydroprocessing

As mentioned in Section 2, the preparation and characterization of supported catalysts developed for petroleum hydroprocessing have been applied accordingly to dispersed catalysts. For example, techniques for the addition of metals introduced as inorganic salts or organometallic complexes onto supported hydrotreating catalysts have been effectively used in the impregnation of these same metals onto coal particles.¹⁵³ This section will also review recent developments in dispersed catalysts for petroleum refining, particularly in the patent literature. The use of coal and other residues as supports, which has direct relevance, will also be briefly reviewed.

3.1.1 Dispersed catalysts for petroleum refining

In Bearden and Aldridge's (1981)¹⁵⁴ Exxon M-coke hydroconversion process, where M-coke stands for micrometallic coke, the catalysts are micron-sized particles which consist of a catalytic metal (Mo preferred) sulfide component combined with a carbonaceous component. They report that as little as 100 ppm Mo can obtain 95% petroleum residuum conversion at 400-454°C and 69-172 bar (1000-2495 psi) total pressures. Catalyst is formed in-situ from oil soluble metal compounds and catalyst dispersion is claimed to be high.

Exxon has numerous patents on dispersed catalysts introduced as soluble (oil- or water-) precursors for heavy oil hydrocracking. Thermally decomposable compounds containing metals from Groups II, III, IV, V, VIB, VIIB, and VIII (preferably Mo, Cr, and V) have been claimed.¹⁵⁵⁻¹⁵⁸ The form of the compounds can be any of the following oil-soluble compounds: carbonyl, halide, inorganic acid, or the salt of an organic acid. In a recent embodiment,¹⁵⁸ the catalyst concentrate is prepared by mixing 565°C⁺ hydrocarbon oil with the metal compounds to provide 0.2-3 wt% metal (based on oil), then heating the concentrate in the absence of H₂ at 275-425°C and 0-35 bar (0-500 psig) for a time to convert to the solid catalyst. The sulfiding agent is elemental S (claimed to be less hazardous than H₂S) and can be used at any stage of the preparation.

Two Exxon patents cover dihydrocarbyl substituted dithiocarbamates of metals of Groups IVB, VA, VIA, VIIA, VIIIA (especially Mo, Fe, Co, and Ni) for hydroconversion of carbonaceous materials, including coal.^{159,160} These precursors do not require sulfiding since they already contain the Mo-S bond. Phillips Petroleum holds several patents on the use of molybdenum dithiophosphates, carboxylates, molybdates, sulfonates, catechols, and mixtures of these compounds.¹⁶¹⁻¹⁶⁴ In addition to superior coke suppression performance, these soluble catalysts can also perform some conversion and upgrading.

In a patent by Lang, et. al. (1989)¹⁶⁵, it is claimed that Group IB, IVB, IVA, VA, VIA, VIIA, and/or VIII metal oxides or sulfides of up to 150 Å on a carbon support are at least as effective as the corresponding metal naphthenate or phosphomolybdate.

The use of organometallic precursors as petroleum hydrotreating catalysts has also been investigated by other groups. Chen, et. al. (1988)¹⁶⁶ studied naphthenates of Ni, Mo, and Co; acetylacetonates of Ni, Mo, Co, V, Cr, and Fe. At 100 ppm, the most active precursors were Ni carboxylate and Mo acetylacetonate. Using %gas yield < %coke yield and %asphaltene conversion as criteria, the relative activities were in the order Ni > Mo > V > Co > Fe > Cr > thermal.

Ojima, et. al. (1985)¹⁶⁷ synthesized molybdenyl acetylacetonate $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$ from MoO_3 and acetylacetone in the presence of water. The use of 500-200 ppm Mo of this precursor gave performance comparable to finely divided Ni-V/ Al_2O_3 (3% on feed) and vanadyl acetylacetonate precursor (1000 ppm V). Ho (1991)¹⁶⁸ prepared his dispersed catalyst by sulfiding tris(ethylenediamine) cobalt molybdate in 10% $\text{H}_2\text{S}/\text{H}_2$ or 1% $\text{H}_2\text{S}/\text{H}_2$ at 400°C for 2 hr. The catalysts were tested for HDS of light cat cycle oil. Steady-state HDS of the catalyst formed by sulfidation in 10% $\text{H}_2\text{S}/\text{H}_2$ was twice that from the catalyst formed in 1% $\text{H}_2\text{S}/\text{H}_2$. The HDN activity difference was small, indicating that sulfur vacancies used for HDN were not the same as those for HDS. Thiotungstosulfonickelate has also been claimed as hydrotreating catalyst precursor.¹⁶⁹

3.1.2 Alkali metal addition

The effect of alkali earth metal addition during the hydrotreatment of petroleum or coal liquids, particularly with respect to coking, has been studied. Masuyama, et. al. (1990)¹⁷⁰ liquefied Australian Victorian brown coal with iron catalyst then deashed the product via extraction with toluene and/or TFF. The deashed coal liquid bottoms was hydrotreated in hydrogenated creosote oil over a commercial NiMo/ Al_2O_3 catalyst. Preasphaltenes deactivated the catalyst probably because N compounds that were strongly adsorbed on the acid sites were converted to coke. Doping the catalyst with Ca (2.7% CaO) resulted in less coke, lower N in the catalyst coke, and stable activity. Baker, et. al. (1987)¹⁷¹, in impregnating aqueous NaNO_2 on Shell 324 M, found that increasing Na reduced surface acidity and decreased coke on the catalyst. Sulfided catalysts, with or without Na, had stable hydrogenation and HDN activities for the hydrotreatment of Pittsburgh coal tar fraction.

The addition of alkali metals has also been used with coal liquefaction catalysts. For example, activity of a Fe-based catalyst promoted with small amounts of other metals like Sn, Mo, Co, Ni, or Zn, can be improved by adding 0.1-0.5 wt% of a Ca compound, preferably $\text{Ca}(\text{NO}_3)_2$.¹⁷² In a German patent,¹⁷³ catalyst prepared from reaction of FeSO_4 with

stoichiometric amount of alkali, such as NaOH (4.5-7.5 pH) has been claimed to be effective at 1.5 wt% addition for the liquefaction of Rhine brown coal at 420°C and 80-500 bar (1160-7255 psi).

3.1.3 Disposable additives in petroleum refining

Coal has been used as disposable additive in several petroleum upgrading processes, such as the CANMET¹⁷⁴ and Veba Oel^{15,16} processes. Both these processes use coal impregnated with an iron-based compound. Bisaria and Bakhshi (1990)¹⁷⁵ used Sheerness subbituminous coal as disposable additive with Mobil Celtic whole crude from Saskatchewan. With no H₂ and catalyst, 20-30% oil conversion was achieved although coking occurred at coal concentrations > 9%. The addition of iron oxide benefitted viscosity reduction and API gravity improvement. As additive, the CANMET process uses up to 10 wt% (usually 5 wt%) coal which has been coated with an iron salt; other coatings that have been claimed in the patent literature include salts of Co, Mo, Zn, Sn, Ni, or W.¹⁷⁴ Concentrations as high as 40 wt% (maf coal) of Forestburg subbituminous have been coprocessed with Cold Lake vacuum bottoms at high severity.^{176,177, 177a}

As with coal liquefaction, clay minerals and spent catalysts have also been investigated as potential disposable additives for petroleum upgrading. Itoh and Tsuchida (1989)¹⁷⁸ used clay minerals and FCC catalysts with Arabian Heavy vacuum residue at 450°C and 85 bar (1235 psi) H₂ (cold). The minerals gave higher yields of middle distillate and lower yields of gum and coke than FCC catalyst, which were impregnated with iron and iron removed from allophane, one of the minerals. The results suggest that iron and macropores are important for suppressing coke formation. Kondo, et. al. (1983)¹⁷⁹ have used spent Co molybdate HDS catalyst with Cold Lake tar sand bitumen. Although the catalyst was active in hydrocracking, the products did not meet fuel specifications.

3.2 Effect/role of sulfur

As mentioned in Section 1.4.2, the sulfide has generally been regarded as the active form for metals that demonstrate catalytic activity during coal liquefaction. Therefore, sulfur, usually in the form of H_2S , elemental sulfur, or dimethyldisulfide (DMDS), is added to non-sulfide catalyst precursors. For example, iron oxide (Fe_2O_3 or Fe_3O_4) alone had no effect but the addition of DMDS or elemental S increased conversion and inhibited retrogressive reactions during the liquefaction of Alberta subbituminous coals by Aitchison, et. al. (1986)¹⁸⁰ or of Zalarroure lignite by Wang, et. al. (1992).¹⁸¹ The use of molten sulfur as sulfiding agent has also been reported.¹⁸²

Even in the absence of catalyst, the addition of sulfur or sulfur compounds has been found to enhance performance. For example, the addition of sodium sulfide¹⁸³ or zinc sulfide¹⁸⁴ has been found to improve coal conversion and the yield of pentane-soluble oils. ZnS addition increased coal conversion from 77% (without catalyst) to 96% and increased oil yield from 16% (without catalyst) to 41%.¹⁸⁴ This improvement has been postulated to be due to the sulfides being free radical initiators and/or sulfiding agents.

The use of H_2S during CANMET corprocessing of Forestburg subbituminous and Cold Lake vacuum bottoms improved both coal conversion and distillate yields at 400-425°C compared to those obtained with Fe (as FeSO_4) impregnation alone. However, at higher severities, FeSO_4 impregnation resulted in better coprocessing performance, possibly due to the stronger hydrogenation activity of FeSO_4 .¹⁷⁶

In a study of coal/oil coprocessing using model coal compounds by Kim, et. al. (1990),^{185,186} excess sulfur enhanced hydrogenation during thermal reactions. This same study also looked at the effect of excess sulfur with catalysts. The MoS_2 catalyst generated from Mo naphthenate with excess S promoted partial saturation of the multiring aromatic to hydroaromatic species but did not promote further saturation of the hydroaromatic or of single-ring alkyl-substituted aromatics.¹⁸⁵ Organic N

compounds deactivated the MoS_2 catalyst; excess elemental S and organic S compounds alleviated this poisoning by the N compounds but inhibited deoxygenation.¹⁸⁶ The addition of sulfur can also help maintain the catalyst in the active sulfided form. Kamia, et. al. (1988)¹⁸⁷ used Fe, $\text{Fe}(\text{CO})_5$, and ferrocene as catalyst precursors with Yallourn brown coal at 400°C. The in-situ water in this high-moisture low-rank coal may reoxidize the catalyst but S addition was found to prevent this.

The organic sulfur content of the coals has also been found to affect the liquefaction performance with dispersed catalysts. Garcia and Schobert (1990)¹⁸⁸ liquefied US Hagel seam, Turkish Cayhıran, and Spanish Mequinenza lignites with or without NH_4 tetrathiomolybdate under several conditions, i.e., N_2 , H_2 , and no solvent. Without the catalyst, conversions and yields for a given lignite were similar regardless of atmosphere; with the Mo catalyst, higher conversions and yields were obtained in H_2 than in N_2 . The liquid yields and increase in yield in H_2 relative to N_2 correlated with the organic sulfur content of the coal. These results suggest that the thermolysis of relatively weak C-S bonds are important in these lignites and that in the absence of a solvent, the dispersed catalyst was important to facilitate hydrogenolysis.

Without external S addition during liquefaction, the organic sulfur content of the coal can also determine the effectiveness of the catalyst. Cook, et. al. (1988)¹⁸⁹ liquefied two Victorian brown coals of similar H/C with different organic S contents: Morwell (0.35 wt% organic S) and Coolungoolum (4.6 wt% organic S). They used aqueous impregnation with Fe acetate or SnCl_2 and liquefaction conditions of 100 bar (1450 psi) H_2 or N_2 (cold) at 300-400°C. Sn was more effective for the low-S coal and Fe was more effective for the high-S coal where Fe was converted to the active pyrrhotite with a 0.92:1 Fe/S ratio and the tin converted to the relatively inactive SnS .

3.3 Sulfated oxides ("superacids")

$\text{TiO}_2\text{-SO}_4^{-2}$, $\text{ZrO}_2\text{-SO}_4^{-2}$, and $\text{Fe}_2\text{O}_3\text{-SO}_4^{-2}$ are among a new type of solid superacids that have been developed for use as catalysts for various acid-catalyzed reactions,^{190, 190a} including coal liquefaction. In a study of the mechanism for the formation of sulfate in sulfur-promoted iron oxide catalysts for coal liquefaction, Kotanigawa, et. al. (1988)¹⁹¹ heated mixtures of pure Fe compounds (such as FeS, FeS₂, Fe₃O₄, and Fe₂O₃) with sulfur and water to 450°C at 2.5 °C/min under H₂ or N₂ at an initial pressure of 101 bar (1465 psi). Both sulfate and sulfide formed simultaneously via reaction of S with H₂O to form SO₂, H₂S, and H₂.

A recent study investigated sulfated zirconia, titania, and alumina with CO and pyridine adsorption and methanol hydration to dimethyl ether as test reactions. Sulfation enhanced the strength of weak Lewis acid sites but poisoned the strong Lewis acid sites. At high sulfate levels, Bronsted acidity was generated.¹⁹⁰

In the generation of acidity on sulfate addition, the acidity has been found to disappear on reduction but reappears on oxidation.¹⁹² Yamaguchi, et. al. (1986)¹⁹³ studied Fe₂O₃ promoted by (NH₄)₂SO₄, SO₃, SO₂, or H₂S. Strong acidity was generated by all promoters as long as the sulfur oxidation state was brought to +6. Different conditions, such as temperature, may be necessary to generate this oxidation state for the various promoters. It is also to be noted that the sulfur species can interconvert between S⁺⁶ and S⁻² by redox treatment. A sulfur oxide species, in which two covalent S=O bonds play an important role, is proposed to be responsible for the generation of strong acidity, although the structure of the acid sites is unclear.

Most of the recent liquefaction work in this area has been done by Pradhan and co-workers at University of Pittsburgh and Kotanigawa and co-workers at the Government Industrial Development Laboratory in Japan. Pradhan, et. al. have investigated Fe oxides and Sn oxides treated with various amounts of sulfate. Liquefaction have been conducted with Illinois No. 6,¹⁹⁴ Blind Canyon bituminous,¹⁹⁵ and Wyodak-Anderson subbituminous^{195, 196} in

tetralin at 400°C and 70 bar (1000 psig) H₂ (cold). They have also studied coprocessing of Illinois No. 6 in Maya atmospheric tower bottoms (1:4 coal:oil ratio) with these sulfated oxides.⁹⁶ Recent work has also investigated bifunctional catalyst systems such as Mo on sulfated iron oxides (Mo/Fe₂O₃/SO₄). Bifunctional 0.5-2.0 wt% Mo on sulfate-promoted ferric oxide, equivalent to 20-100 ppm Mo on coal, has been found to give performance comparable to or better than that obtained with the sulfated oxides.^{96,97}

In general, sulfate addition resulted in promotion of coal conversion and oil yield. Sulfated iron oxides were significantly more active than the unsulfated oxides.¹⁹⁶ For example, use of <0.7 wt% sulfated ferric oxide gave 86% maf coal conversion with >50 wt% pentane-soluble oil in the liquefaction of Illinois No. 6. Moreover, elemental S added to this catalyst further increased both coal conversion and oil yield (90% and >60%, respectively); similar results were obtained with sulfated SnO₂.¹⁹⁴ The bifunctional Mo/Fe catalysts were more active than the sulfated Fe oxides and Sn oxides. For example, in the coprocessing study, a bifunctional 3500 ppm Fe + 50 ppm Mo catalyst gave higher coal conversion (78%) and oil selectivity (80%) than those obtained with ferric sulfate and the catalyst precursors Fe(CO)₅ or Mo(CO)₆. The order of catalyst activities at 400°C, based on the yields of pentane soluble products was bifunctional > sulfated Fe₂O₃ > Fe(CO)₅/Mo(CO)₆ > Mo(CO)₆ > Fe(CO)₅. It is postulated that the Mo contributed hydrogenation function, and that the sulfate ion possibly prevented sintering or agglomeration of the bifunctional catalyst.^{96,97}

This sulfate promotion has been attributed to an increase in catalyst dispersion and surface acidity.¹⁹⁴ In a study of finely-divided FeOOH, Fe₂O₃, and Mo/Fe₂O₃ containing 3-4 wt% sulfate ion (with elemental sulfur for sulfidation), the surface areas increased and particle sizes decreased on sulfate addition. This facilitated conversion of the oxides to the active sulfide phase. Moreover, Mo was more effective with calcined sulfated iron oxide than with its uncalcined form.¹⁹⁵

The effects of the sulfate group in these oxides may be due to an increase in catalyst dispersion, a (probable) inhibition of agglomeration of the metal oxide catalysts at the high temperature, and superacidity of the surface. The superacidity attained with sulfate promotion also achieved significant HDN and HDS. A small amount of moisture in the catalyst system helps maintain high acidic activity, maybe due to transformation of the catalyst to its Bronsted acid form, responsible for generating carbocations. The pyrrhotites formed from iron in coal had a much larger particle size ($d_{avg} = 30$ nm) than that formed from iron added as sulfated iron oxide (10 nm).¹⁹⁷

The Japanese work with sulfated oxides has also been conducted with coals of various ranks: Taiheyo bituminous,¹⁹⁸ Akabira bituminous,¹²⁶ and Yallourn Australian lignite (which contains no pyrite).¹²⁶ Liquefaction experiments have been conducted in tetralin at 100 bar (1450 psi) H_2 or N_2 (cold) with FeS_2 , $Fe_2O_3(SO_4)^{-2}$, and $(NH_4)_2SO_4$ as catalysts. With Taiheyo, FeS_2 and $Fe_2O_3(SO_4)^{-2}$ gave similar coal conversions; however, bifunctional FeS_2 - $Fe_2O_3(SO_4)^{-2}$ gave excellent results.¹⁹⁸ Fe_2O_3 with 1.2% added sulfate had highest activities for hydrogenation and hydrocracking of tetralin for Akabira and Yallourn coals although HDN and HDO activities were not very good. FeS_2 showed slightly lower activity (was active only for Akabira) and $(NH_4)_2SO_4$ was inactive for both coals (only showed activity for hydrogenation of tetralin). These results indicate that the catalytic action is via reaction with H_2 rather than through participation of the donor solvent.¹²⁶ A Japanese patent issued to the Agency of Industrial Science and Technology¹⁹⁹ claims coal conversions of up to 79% with FeS - $FeSO_4$ or $FeSO_4$ sulfated on an Fe oxide composite. The patent also claims that addition of $(NH_4)_2SO_4$ can accelerate hydrogenation.

3.4 Multicomponent catalysts

In coal liquefaction, the need for both hydrogenation and cracking functionalities may be achieved with multicomponent catalysts. For example, tin, which has been used in commercial coal liquefaction

developments along with molybdenum and iron, has been found to be very active in combination with HCl or HI²⁰⁰, although this caused corrosion problems. Maa, et. al. (1989)²⁰⁰ claim that tin and iodine (as HI) are effective for coal hydroconversion, preferably at 70-207 bar (1000-3000 psig) total pressure and 56-172 bar (800-2500) psig H₂; higher naphtha is obtained if sulfides of metals other than Sn added. Sn + NH₄Cl has also been found to be effective as a bifunctional catalyst with both cracking and hydrogenative functions.²⁰¹

A special case of multicomponent catalysts is that of bimetallic catalysts; Cusumano, et. al.⁵⁸ have a good (although old, 1976) review. The points brought out in the review could be extended to nonmetallic catalysts, i.e., sulfides. Although catalyst systems with two or more components (metals) have been disclosed or discussed in the patent or open literature, bimetallic systems are best understood. The earliest approach to their study has looked at their electronic properties with the view that control of the density of d-electrons was instrumental in explaining their properties. Since then, other models have provided better pictures. Moreover, recent developments in characterization techniques have shown that surface and bulk compositions of these catalyst can differ significantly. These bimetallic catalysts can be supported or unsupported, with the latter easier to study and characterize. Supported catalysts occur as alloys or metal clusters; they are usually supported on high-surface area materials since it is difficult to maintain highly-dispersed metals in the unsupported state without sintering and crystallite growth. The general observation is that supported metal catalysts are more stable than unsupported metal catalysts with respect to sintering.

The combination of two metal catalysts can result in promotional effects and better activity maintenance; in the latter case, alloy formation can increase resistance to coking by diluting primary active centers, or by properly balancing hydrogenation and cracking activities. Alloying can also enhance selectivity; for example, alloying with an inert metal can enhance selectivity to products which require single sites and can decrease formation of products from pathways requiring several contiguous

active metal sites. It is to be noted, though, that during coal liquefaction conditions where high concentrations of H_2S may be present, the catalyst system is a mixture of sulfides, and not of the metals. The sulfides may also occur as mixed sulfides. Diaz, et. al. (1990)²⁰² performed an X-ray diffraction study of a CoMo sulfide formed by the decomposition of a thiosalt. Their analysis indicated the presence of a mixed Co-Mo sulfide in addition to the MoS_2 and Co_9S_8 phases.

A special class of multimetallic catalyst systems is the ultrastable intermetallic compound which is an alloy of two or more metals that has a characteristic crystal structure and definite stoichiometry. It usually consists of two metals from opposite ends of the periodic table (e.g., ZrIr_3 , ZrPt_3). It is difficult to prepare the more stable ones because of the high temperatures needed for the alloying.

The promotion of supported catalysts with soluble catalysts has also been investigated. Work at SRI by Hirschon and co-workers^{98,203} have been investigating promotion of supported CoMo, NiMo, and WMo with soluble Ru carbonyl. Ru exhibited a synergistic relationship with Mo. $\text{RuCoMo} > \text{RuNiMo} > \text{RuNiW}$ in terms of activity but $\text{RuNiW} > \text{RuNiMo} > \text{RuCoMo}$ in terms of selectivity. In terms of conversion to THF-solubles, RuCoMo was more effective in the liquefaction of Wyodak coal in tetralin than CoMo; RuCoMo was also more effective than unpromoted CoMo in HDN of coal liquids.

In Section 3.3, the use of bifunctional dispersed Fe+Mo was briefly discussed in sulfated oxide catalyst systems. Combinations of metals other than Fe+Mo have been investigated. Table 7 lists some of the combinations, mostly from the patent literature. The promotion of Fe with other metals will be discussed in greater detail in Section 5.3.

4. CATALYSIS BY MOLYBDENUM

Petroleum hydroprocessing catalysts containing transition metal sulfides have been widely used in HDS, HDN, and product quality improvement (hydrotreating). Original interest (pre-WWII) in these catalysts were in their activity for hydrogenating high-sulfur coals (hence maintaining the metal in the sulfided state). Co, Ni, Mo, and W sulfides and their mixtures were most active and least expensive; after WWII, major uses shifted to Co- and Ni-promoted Mo and W catalysts usually supported on Al_2O_3 . Unfortunately, there is still little understanding of the basis for and origin of catalytic activity.

This section provides a more detailed discussion on Mo-based dispersed catalysts, MoS_2 (chalcogenides), and liquefaction results with various precursors. It also discusses oil-soluble Molyvan as a coal liquefaction catalyst, and the promoting effect of phosphorus, based on resid hydroprocessing/hydrotreating work on alumina-supported Mo catalysts.

4.1 Morphology and properties of MoS_2

MoS_2 from low-temperature precipitation is amorphous, but highly disordered rag-like morphology can develop when MoS_2 is annealed in $\text{H}_2\text{S}/\text{H}_2$ at 400°C . It has a high surface/volume ratio. Weak bonding between adjacent basal planes leads to "lubricity", which results in MoS_2 's intercalative properties that have found it applications in electronics, for example. MoS_2 (and WS_2 to lesser extent) have HDS and HDN activity; the edge plane has been proposed as the source of this activity.

Chianelli and co-workers²⁰⁴⁻²⁰⁷ have reviewed the properties of MoS_2 , particularly as it relates to petroleum hydroprocessing. In general, the catalytic activity, e.g. for hydrodesulfurization (HDS), can be correlated with the electronic configuration of the d-orbitals as "percentage d character" of the metallic bond (based upon Pauling's valence bond theory) or with the strength of the metal adsorbate bond. A relation among HDS activity, heat of adsorption of a reacting molecule, and heat of formation

of the corresponding sulfide exists (Sabatier's principle), i.e., compounds exhibiting maximum activity will have intermediate heats of formation, presumably because the stability of the surface complex formed by the sulfur-bearing molecule will be intermediate. The metal-sulfur bond at the surface of the catalyst must not be too strong or too weak to obtain maximum HDS; this appears consistent with idea that sulfur vacancies on catalyst surface are active HDS sites (but this is not the entire picture). Some electronic factors, such as number of electrons in the highest occupied molecular orbital of each cluster and relative metal-sulfur d-p covalent strength, provide a basis for the observed trends in catalytic activity but there is still a need to define a relation between these factors (which are based on bulk electronic structure of the metal sulfides) and the electronic structure of active sites on the catalyst surface (i.e., need to define relation between bulk and surface electronic structures).

In the determination of catalyst activity, geometric properties, such as crystal structure, appear to be of secondary importance. Heat treatment conditions can be optimized to obtain highest activity. For example, for anisotropic MoS_2 , HDS activity does not correlate with surface area, but does with O_2 chemisorption. However, for isotropic RuS_2 (cubic), linear correlations between HDS activity and both surface area and O_2 chemisorption exist. There is indication that the edge plane of MoS_2 is active but this cannot be confirmed by single-crystal studies since MoS_2 can only be grown in very thin crystals which do not permit study of edge planes.

The structural nature of the active site and the concentration of these sites on the edge plane are chemical properties that may affect catalyst activity. ESR has been used to characterize the defect sites; one work has correlated defect site density with activity for benzene hydrogenation over WS_2 catalysts.

Promotional factors, such as the presence of a second metal, can result in activities greater than the sum of activities of the two catalysts, as discussed in the section on multicomponent catalysts. No consensus exists

as to the origin of this synergistic effect, although there appears to be a relation between the activity of these synergic pairs and the average heats of formation of the sulfides of the pairs. Elements to the left of the periodic table have high heats of formation, bind sulfur too strongly, and are poisoned by sulfur; those to the right have low heats of formation and sulfur-containing molecules are too weakly bound for reaction to take place. Averages of these heats of formation can fall into the optimum range; examples are Co/Mo, Ni/Mo. In the case of Fe, if the heat of formation of FeS_2 is used, then Fe/Mo average heat of formation falls outside the optimum range, suggesting no synergy. However, recent work (discussed in Sections 3.3 and 3.4) indicate synergy; this suggests that the active form may not be FeS_2 .

In general, surface areas of synergic pairs are lower than those of the pure phases; this suggests that the number of active sites is not increasing but rather that the quality of the active site may be enhanced. Microscopic theory for promotion suggests that somewhere at the edge, sulfur atoms (which upon leaving create vacancies) are shared by the metals (promoter and Mo for example) and behave in an average electronic fashion, i.e., metal-sulfur bonds are adjusted to intermediate values which are necessary for high activity.

4.2 Molybdenum catalysts and precursors

As discussed in examples in Section 2, molybdenum has been introduced in the form of MoO_3 , MoS_2 , and MoS_3 fine powder, soluble organometallics (such as Mo naphthenate, octoate, carbonyl, acetylacetonate, oxalate), phosphomolybdic and molybdic acid, oil-soluble Molyvan additives, and water-soluble molybdates (ammonium molybdate, AHM, and ATM). The relative effectiveness of these precursors depend on the coal and liquefaction conditions. In general, the soluble precursors result in improvements in coal conversion and oil yield compared to no catalyst or to the use of fine powder Mo oxides or sulfides. An exception to the latter case is the use of nanometer-sized particles. Tables 6a and 6b lists selected

references for the studies on molybdenum-based dispersed catalysts, most of which have been discussed in Section 2.

The high activity of Mo-based catalysts are of particular interest in the liquefaction of low-rank coals. Derbyshire and co-workers have found that low-rank coals can be liquefied to obtain similar to higher yields than bituminous coals (even at lower temperatures) if the coals are vacuum-dried to ~4 wt% moisture at room temperature and then heated slowly to liquefaction (>400°C). This mild pretreatment is necessary to prevent cross-linking reactions that normally occur during coal drying and heat-up prior to liquefaction.²⁰⁸⁻²¹⁰ Similar improvements were observed with coals that had been impregnated with water-soluble Mo precursors, such as NH_4 tetrathiomolybdate. For example, the highest yields of chloroform-solubles during liquefaction with no solvent at 350-400°C in 70 bar (1000 psig) H_2 (cold) for 1 hr was obtained from subbituminous coals and the least was for a low-volatile B bituminous coal.²⁰⁸

Cugini and co-workers at DOE have also used AHM and ATM as catalyst precursors in coprocessing. In the coprocessing of 0-30% Illinois No. 6 with North Slope vacuum resid, Boscan, or Maya atmospheric resid at 84 bar (1200 psig) H_2 (cold) and 425°C for 1 hr, the addition of 0.1-1.0 wt% Mo as AHM increased yields of heptane solubles.³⁶ In a more recent study of the coprocessing of Illinois No. 6 or Ohio No. 5/6 in process-derived H donor solvent or with Maya atmospheric residuum or Cold Lake vacuum residuum at 420-450°C and 173 bar (2500 psig) H_2 for 0.5-1.5 hr, high catalyst activities were obtained with the addition of up to 1000 ppm Mo (based on coal), added as ATM or MoS_3 .²¹¹

Other metals can be added to Mo as co-catalysts, as seen in Table 7. For example, a Japanese patent claims good removal of S and metals at 100-1000 ppm Co, Ni, Fe, V, Ti, Zn, Cu, or W added to Mo as co-catalyst.²¹² Koo, et. al. (1992)²¹³ studied various bimetallic systems and found that bimetallic Mo-P/ RuCl_3 - H_2O offered the highest activity.

4.3 Mo-S-P catalysts

In supported MoS_2 - $\gamma\text{Al}_2\text{O}_3$ hydrotreating catalysts, the active phase consists of small slabs of MoS_2 , generally well-dispersed on the support, with the coordinatively unsaturated Mo edge atoms considered as the active sites. The addition of phosphorus generally improves catalytic performance of Al_2O_3 -supported MoS_2 catalysts but it is a poison for C-supported ones. Poulet, et. al. (1991)²¹⁴ reviews the effects of phosphorus on alumina-supported MoS_2 catalysts; in general, the effects are in morphological changes in the MoS_2 and/or the support and in the surface properties of the support. This section will review those effects that may be relevant to dispersed MoS_2 catalysts.

The direct effects of phosphorus addition on the MoS_2 active phase are probably the most relevant to dispersed catalysts. One effect may be the direct replacement of some sulfide species by phosphide-like species which can induce modification in the site structure. Another effect is that of the P-O-Mo bridges on the ordering of the stacked MoS_2 layers.

- 1) Alteration of the stacking of MoS_2 layers
-- More stacked layers of MoS_2 have been observed when P is present. This may be due to the different (i.e., weaker) interaction of MoS_2 with the support surface. If the stacked platelets have irregular superposition, there may exist a diffusion limitation for the reactants to reach the active sites.

In the electron microscopy study by Ramirez, et. al. (1992),²¹⁵ P addition to the supported catalysts with low Mo promotes formation of single- and double-layered MoS_2 when P and Mo are impregnated simultaneously. P addition before Mo impregnation resulted in higher stacking of the MoS_2 crystallites and promoted formation of partly sulfided MoO_3 particles. Moreover, P addition to catalysts with high Mo prevented agglomeration of MoS_2 particles.

2) Change in the coordination of the sites

-- In the case of catalysts where Ni is present along with Mo, the interaction of P with the active Mo sites can induce changes in the site coordination of both Mo and Ni. For example, in an FTIR and NMR study of supported Mo by DeCanio, et. al. (1992),²¹⁶ the addition of up to 1.5 wt% P promotes the formation of reducible octahedrally coordinated molybdena on the alumina surface. The electron density of the site is modified as well. The addition of >2.0 wt% P results in formation of bulk MoO_3 and $\text{Al}_2(\text{MoO}_4)_3$. It is postulated that the presence of low amounts of P causes an increase in the number of sites adsorbing CO and increasing P further decreases the number of these adsorbing sites, probably due to the formation of either Ni phosphate or Ni molybdate.

The trend of increase in number of CO-adsorbing sites with P addition up to a maximum was observed by Kushiya, et. al. (1991)^{217,218} in the HDS of Morichal Venezuelan crude at 470°C using the soluble catalyst precursors Mo naphthenate, Co octylate, and di-2-ethylhexylphosphate. (H_2S generated from elemental sulfur addition can accelerate decomposition of the precursors below 240°C.) P addition increased HDS activity up to a maximum and this optimum level was unchanged by Mo concentration. The improvement was attributed to the formation of oil-insoluble P-V compounds that separated from the active Mo-Co-S phases. This interaction of P with V also led to better hydrodevanadation, thereby preventing catalyst deactivation by V. Excess P can poison the catalyst, though.

3) Change in the acidic properties of the (coal) support

-- Depending on the P loading and the structure of the surface phosphates, acidity can be increased or decreased. Lewis sites may be created by elimination of H_2O and/or H_2S from the surface OH and/or SH groups upon P treatment. Lower coke yields have been reported with phosphorus addition.

4) Enhancement of dispersion of metals

-- In a recent study of thiophene HDS using $\text{MoO}_3\text{-Al}_2\text{O}_3$ hydroprocessing catalyst promoted with 0 or 1 wt% P, Al-OH groups were more reactive toward molybdena, resulting in higher Mo dispersion for the P-promoted catalyst.^{219,220}

4.4 Oil-soluble Molyvan additives

Oil-soluble Molyvan additives, marketed by Vanderbilt Inc. as commercial anti-oxidant and anti-friction agents for engine lubrication, have recently been investigated as coal liquefaction catalysts. Molyvan L and Molyvan 822 are two such additives which already contain Mo-S bonds so that no sulfiding is necessary. Phillips Petroleum has investigated their use as catalysts and coke suppressants during resid hydroconversion.¹⁶¹⁻¹⁶⁴

Swanson (1992)¹⁰⁶ studied the liquefaction performance of oil-soluble Molyvan L (molybdenum di-2-ethylhexylphosphorodithioate in mineral oil) in a Wilsonville-type two-stage process. In this study, Molyvan L and sulfided Mo octoate both gave high Illinois No. 6 residuum conversion although the distilled fractions contained more heteroatoms that must be removed by subsequent hydrotreatment.

The performance of Molyvan additives in combination with supported catalyst has been tested in the close-coupled integrated mode at the Wilsonville coal liquefaction facility.¹⁰⁷ Solids buildup can be a problem during subbituminous coal operation so the potential use of these Molyvan additives in the maintenance of low coke levels was investigated with Black Thunder subbituminous coal. The addition of 100 ppm Mo (on moisture-free coal) as Molyvan L or Molyvan 822 with or without Criterion 324 unimodal supported catalyst was tested. With the additive alone, both coal and residuum conversions were increased so that operation at lower thermal severity in the first stage and higher thermal severity in the second stage (compared to with the supported catalyst) was possible. With the hybrid (dispersed Mo + supported catalyst) system, C_4^+ distillate

product yields increased 30-60% compared to that with either of the individual catalysts. Distillate product quality was similar to that obtained with supported catalyst alone, although of higher quality than that obtained with the dispersed Mo alone.

5. CATALYSIS BY IRON

Although Mo, in general, has higher activity compared to Fe, Fe-based catalysts, such as pyrite, have the advantages of a disposable catalyst -- low cost, availability and environmental compatibility. The relative low activity of Fe may be improved by methods that can modify its compositions. A composition modification reported to increase activity of iron-based catalysts is mixing different forms of iron. For example, a mixture of Fe oxide and pyrite increases oil yields to 39% from the maximum of 27% attainable with the catalysts separately.²²¹ Greater activity enhancements are possible; Derbyshire and Hager (1992)²²² review some of these methods such as sulfation to change surface properties, promotion with low concentrations of other metals (such as Mo, Ni, Ti), and formation of intermetallic hydrides which can store H₂. Sulfated oxides and promotion in multicomponent catalysts have been discussed previously in this review.

Increasing the surface area of iron oxide catalysts can also improve hydrogen incorporation, although oil production is not substantially improved.²⁷ For example, Stohl (1983)²²³ studied various forms of FeS_x -- synthetic FeS₂ (46.6 wt% Fe) of 2-10 m²/g areas, FeS_x (60 wt% Fe) of 6 and 10 m²/g areas, and iron sulfides of unknown composition of 40 and 80 m²/g areas. In the liquefaction of W. Va. Blacksville No. 2 in SRC-II heavy distillate, catalytic conversions were to a lesser extent than those obtained with Co-Mo/Al₂O₃. Moreover, although surface areas changed drastically during heat-up, no large differences in conversion among these catalysts were observed.

5.1 Reaction mechanism

Cook and Cashion (1987)¹³⁸ summarized the prevailing (sometimes contradictory) ideas on the role of iron during coal liquefaction at that time. Based on some early 1982-1983 studies by Cassidy and others with coal model ethers where adsorption of phenoxy radicals on iron surfaces was observed, it was inferred that iron slows the propagation of coal

radicals that were initially formed during liquefaction. Hence, because these retrograde reactions are reduced, more asphaltene is formed. The activity of iron in coal conversion was, therefore, thought to be confined mainly to asphaltene production rather than subsequent upgrading to oil. Moreover, iron appeared to influence mechanistic steps not associated with the solvent. Brooks, et. al. (1984)²²⁴ studied liquefaction at longer residence times and determined that pyrite accelerated coal conversion to (pentane-soluble) oils, although the effects on other product fractions were less pronounced. Moreover, their model compound work suggested that pyrite catalysis involved acceleration of both direct hydrogenation reactions involving molecular H₂ (e.g., replenishing solvent hydroaromaticity) and reactions involving H-transfer from donor solvent. Thus, iron appears to effect both short-term reduction and long-term enhancement of coal conversion.

Farcasiu, et. al. (1991)²²⁵, in testing various Fe compounds with a model compound 4-(1-naphthylmethyl)bibenzyl, found that non-stoichiometric Fe-S compounds can selectively catalyze cleavage of C-C bonds between condensed polyaromatic moieties and aliphatic carbons. The nature of the active sites was found to depend on the water content of the catalysts: without water, the reaction was of an ion-radical type mechanism, whereas with water, the reaction was of an ionic mechanism.

In a spectroscopic study of depolymerization with an iron-based catalyst of coal macerals from Hiawatha Utah coal, Wang, et. al. (1992)²²⁶ determined that the iron catalyst was evenly dispersed inside vitrinite and that this uniform dispersion was preserved upon mild hydrotreatment. Iron did not completely penetrate into the resinite due to lack of microporosity.

Although not generally regarded as a good hydrogenation catalyst, iron possesses hydrogenation capability. A catalyst prepared from the reaction of Fe₂O₃ with H₂S at 260-315°C in a non-oxidizing atmosphere or at 350°C in a H₂ atmosphere and stored in inert atmosphere before use, has been claimed to have high activity for hydrogenating polycyclic aromatics in coal liquids.²²⁷

Based on the above studies, for liquefaction of low-rank coals, where initial retrogressive reactions can limit conversion, iron may catalyze cracking to form radicals which must be capped by a good donor solvent and/or a good hydrogenation catalyst in order to get good conversion. For example, subbituminous coals such as Wyoming Black Thunder have been successfully liquefied at the Wilsonville coal liquefaction facility with pyrite (+DMDS) + supported catalyst. High conversions and yields have also been obtained with pyrite + oil-soluble Molyvan L. Wilsonville experience has shown that the addition of iron as pyrite is almost necessary for a high level of liquefaction of low-rank coal, although the actual mechanism is still unknown. Good dispersion of iron may be achieved with low-rank coals. Aggregation of iron atoms can occur more readily over bituminous coals than lower-rank coals at the same loading because low-rank coals have more surface functional groups that can interact with the iron.²²⁸

5.2 Pyrrhotite as active form

Table 8 shows the various crystalline phases in the Fe-S system. Pyrrhotite (Fe_{1-x}S) is the stable form during coal liquefaction conditions and the general consensus is that it is the catalyst active form. Mixing pyrrhotite in with coal did improve liquefaction over thermal but not as much as when pyrrhotite is produced in-situ from pyrite decomposition. This difference may be due to the more intimate contact between coal and the coal-derived pyrrhotite. It can also be due to the difference in morphology between pyrite in coal vs. synthesized pyrite.

There have been numerous studies to determine the active form of the iron catalyst during liquefaction, using model compounds and coals (see Table 4b). In their model compound investigations, Suzuki, et. al. (1989)²²⁹ used the following iron catalyst precursors: $\text{Fe}(\text{CO})_5\text{-S}$, FeS_2 , and Fe_2O_3 . Active carbon was added to simulate coal and to improve dispersion; $\text{Mo}(\text{CO})_6\text{-S}$ was also used for comparison. The model compound reactions studied were the hydrogenation (with decalin) of phenanthrene and pyrene, and the hydrogenolysis (without solvent) of diphenylmethane, dibenzyl

ether, and biphenyl ether. Mossbauer spectroscopy on $\text{Fe}(\text{CO})_5\text{-S}$ deposited on active carbon from hydrogenolysis of diphenylmethane showed pyrrhotite and an unidentified doublet peak that was not seen for the other Fe-S catalysts. This catalyst (and the $\text{Mo}(\text{CO})_6\text{-S}$) showed higher catalytic activity than the other catalysts. This doublet peak (the definite species of paramagnetic iron giving this peak is not known) may be responsible for the higher activity of $\text{Fe}(\text{CO})_5\text{-S}$. It is to be noted that the spectrum of $\text{Fe}(\text{CO})_5$ without S indicated Fe metal and cementite.

Olson and Yagelowich (1992)²³⁰ formed pyrrhotite from calcination and sulfidation of iron-pillared clays. During hydrocracking and hydrogenation test reactions with bibenzyl and pyrene, respectively, the presence of pyrrhotite resulted in minimal coking and condensation reactions. The iron tended to migrate from its originally dispersed state as surface area decreased as the layers collapsed.

In the coal liquefaction studies, the initial form of the iron catalyst is usually as an oxide. Huffman, et. al. (1992)²³¹ studied the precursors sulfated Fe_2O_3 , iron added by chemical impregnation, and iron added by ion exchange. In their as-dispersed state, all were in the form of superparamagnetic ferric oxides or oxyhydroxides. Djega-Mariadassou, et. al. (1986)⁸¹ observed pyrrhotite stoichiometries (1-x) of 0.87 and 0.90 after hydrolquefaction of sulfided Fe_2O_3 aerosols prepared by a flame method. Moreover, the hexagonal habit was preserved as pyrite transformed to pyrrhotite; this may explain the absence of sintering. Srinivasan, et. al. (1992)²³² characterized iron oxide and sulfided iron oxide catalysts generated from Fe_2O_3 precursor with 300 m^2/g surface area under simulated coal liquefaction conditions. Sulfidation was at 385°C. The majority of the diffraction patterns in the electron microdiffraction analysis corresponded to the Fe_7S_8 phase. Ferric naphthenate sulfided at the same conditions yielded catalysts of a different morphology containing FeS_2 , FeS , and Fe_7S_8 . There was no evidence for the presence of Fe metal.

In the examples above, the catalyst precursors were sulfided. If no additional source of sulfur is provided, the form of the iron catalyst during liquefaction conditions can depend on the precursor and the Fe-S

ratio in the coal. Cook and Cashion (1987)¹³⁸ liquefied Morwell Victorian brown coal using <40 μm hematite ($\alpha\text{-Fe}_2\text{O}_3$) powders physically mixed with the coal and $\text{Fe}_3(\text{CO})_{12}$. For this coal, which had $\text{Fe/S} \sim 3$, it appeared that FeS was the active species for the Fe_2O_3 precursor for long residence times (they proposed an ionic divalent species which stabilizes radicals during short residence times). For brown coals with $\text{Fe/S} \sim 0.3$, such as Loy Yang and Coolungoolun), they report that pyrrhotite was formed. They proposed the following iron transformation: rapid reduction from FeOOH via a transient divalent species to magnetite (Fe_3O_4). When H_2 is present, magnetite is further reduced to elemental iron, which in turn forms Fe_3C ; inherent or added sulfur reacts with Fe_3O_4 to form FeS or Fe_{1-x}S . For Fe carbonyl, they proposed that elemental Fe may be the active form, promoting coal hydrocracking and producing Fe_3C in the process. Yamashita, et. al. (1989)²²⁸, in their investigation of Loy Yang impregnated with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ also proposed a similar iron transformation scheme. Based on Mossbauer, XAFS, XANES, and XRD analysis of the liquefaction residues, the following scheme is the proposed progression of the iron species: highly dispersed iron species to ultrafine FeOOH, and then crystalline reduced species ($\alpha\text{-Fe}$, $\gamma\text{-Fe}$, Fe_3C , depending on iron loading).

5.3 Promotion by other elements

Section 3.4 presented a general discussion of the principles involved in multicomponent catalysis. The promotion of Fe coal liquefaction catalysts with other elements is the subject of many patent claims. In one of them, Kleppel, et. al. (1987),²³³ mixes coal containing a fine iron compound, i.e., oxide, hydroxide or hydrated oxide, with Ni, Mn, Cr, Mo, W, Ti, Al, and/or Sn, and with a P-containing oil (0.03-3 wt% in form of organophosphorus compounds). It is claimed that the P increases distillate yields without causing excessive corrosion from phenols. Table 7 lists other patents and investigations on the promotion of Fe-based catalysts with small amounts of other metals, primarily Groups VI or VIII such as Mo, Sn, Mn, and Ru.

Promotion of dispersed Fe catalysts by Mo has been actively pursued recently. Garg (1984)²³⁴ reports that during liquefaction at 400°C, conversion to oil with 1% Fe (added as FeSO₄) and 0.02% Mo (added as NH₄ molybdate) is 36% compared to 25% with 1% Fe alone. During the liquefaction of high-volatile Freyming bituminous coal, Bacaud (1991)^{32,235} improved the effectiveness of iron oxide aerosols produced by a flame method by the addition of small amounts of Mo. Asahi Chemical Industries claim improved liquefaction rates and oil production and less gas generation with Fe promoted by Mo or other metals (Co, Ni, W, Ti, Sn, Zn, V, Cr, and Sb).^{236a,b,c}

The addition of low amounts of Mo (20-100 ppm on coal)⁹⁶ to sulfated Fe oxide resulted in improvements in coal conversion and oil yield which was partially attributed to the contribution of hydrogenation function by Mo. Davis, et. al. (1988)²³⁷ also looked at a bifunctional Fe+Mo catalyst. A high-volatile C coal (PSOC-1498) was impregnated with Mo, Fe, or Fe+Mo using NH₄ heptamolybdate and NH₄ tetrathiomolybdate. The bimetallic Fe+Mo catalyst was very effective for liquefaction with or without a low-boiling recycle solvent. In terms of total conversion and H₂ consumption, the order of activity (without solvent) was 1% Fe+0.1% Mo ~ 1% Mo >> 1% Fe; a similar relative activity order was obtained during liquefaction with solvent. Miki, et. al. (1992)¹³⁷ also found that the addition of small amounts of soluble Mo to ion-exchanged iron on Taiheyo resulted in higher activity than that from either Mo or Fe alone.

Cook and Cashion (1988)²³⁸ investigated catalysis by Fe+Sn with a Victorian coal (from which quartz and pyrite/marcasite has been removed) which was treated with aqueous FeSO₄/SnCl₂ solutions, then dried under N₂ at 105°C. Although there was no evidence of association between the initial ferric and stannic species, some FeSn₂ formed during liquefaction. Tin accelerated the formation of iron sulfide while iron retarded the formation of tin sulfide during initial liquefaction. Tin also prevented the carbiding of elemental α -Fe to Fe₃C.²³⁸ High liquid yields have been claimed using an FeSn sulfided catalyst prepared by dissolving Fe in an HCl solution containing Sn halides or organohalides at a Fe:Sn ratio >

3.²³⁹ Effective FeSn catalysts have also been prepared by flame decomposition of FeCl_3 and SnCl_4 .⁸⁰

Wallach, et. al. (1990)²⁵ claim a disposable Fe+Mn catalyst formulation containing 5-25 wt% Fe, 15-25 wt% Mn, and 8-12 wt% S for coal liquefaction at 200-500°C, 50-400 bar (725-5800 psi) for 15-200 minutes. The Fe and Mn are preferably in oxide, hydroxide, or sulfate forms and added in a concentration of 0.2-5 wt% based on the feed. In a patent issued to the Agency of Industrial Science and Technology (1991)²⁴⁰ in Japan for an Fe+Ru catalyst, FeS_2 impregnated with RuCl_3 at 120°C (0.013 wt% Ru in catalyst) can conduct liquefaction at moderate conditions, compared to FeS_2 .

Table 1. German Commercial Coal Liquefaction Plants, 1944
(Adapted from Donath, ref. 4)

Start-up	Location	Owner	Feed	Catalyst (1 st stage)	P, psi (1 st stage)	Product	Product capacity (10 ³ t/yr)
1927	Leuna	ICI Farben- industrie (licensee)	Brown coal, brown coal tar	Mo	200	Motor fuels	650
1936	Boehlen Magdeburg	Braunkohle Benzin AG	Brown coal tar	Mo	300	Motor fuels (char by-product)	250 220
1939	Zeitz		Brown coal tar	Mo	300	Motor fuels, lube oils, paraffin wax	280
1941	Wesseling	Rheinische Braunkohle	Brown coal	Fe	700	Motor fuels, diesel fuel	250
1942	Brux		Brown coal tar	Mo	300	Motor fuels	600
1936	Scholven	Hibernia AG Mining Co.	Bituminous coal	Sn-HCl	300	Motor fuels	280
1937	Welheim	Stinnes AG	Coal tar pitch	Fe	700	Motor fuels	130
1939	Gelsenberg	Vereinigte Stahlwerke AG	Bituminous coal	Fe	700	Motor fuels	400
1940	Poelitz		Bituminous coal oils	Fe	700	Motor fuels	700
1940	Luetz- kendorf	Wintershall AG	Tar oils	Fe	500	Motor fuels	50
1943	Blech- hammer		Bituminous coal tar, pitch	Fe	700	Motor fuels, navy fuel oil	420

Table 2. Some Disposable Catalysts for Coal Liquefaction (Other than Coal Minerals)

ORES AND ORE CONCENTRATES:	Active component(s)	References
Pyrite	Fe	Mathur, et. al. (1984) ⁸ , US Patents ^{12,13}
Limonite	Ni, Fe	Mathur, et. al. (1984) ⁸ , US Patent ¹³
Bauxite	Al	Mathur, et. al. (1986) ⁹
Laterite	Ni, Fe, Al	US Patent ¹²
Manganese nodules	Mn	US Patents ¹⁰⁻¹²
Ore tailings	Fe	German Patent ²⁵
MoO ₃ ore	Mo	Mathur, et. al. (1986) ⁹
MANUFACTURING RESIDUES:		
Red mud	Fe	Donath (1982) ⁴ , Sato, et. al. (1987) ²⁶ , German Patents ¹⁶⁻¹⁸
Lithopone production waste	Zn, Fe	German Patents ¹⁹⁻²¹
Coal liquefaction and/or residuum hydroprocessing residues	Fe, Mn	German Patent ²⁴
Galvanic slurries	Ni, Zn, Cr(III), Cu	German Patent ¹⁹
Leather industry waste water	Cr	German Patent ¹⁹
Electrochemical metal processing waste water	Zn	German Patents ^{19,21}
Spent catalyst	Fe	Japanese Patent ²²
Blast furnace flue dust		US Patent ²³
Production wastes from plastics, fungicides, anti-fouling agents	Sn	German Patent ²⁴
Pigment production wastes	Fe	German Patent ²³

Table 3. Effect of Catalyst Dispersion on Liquefaction Performance
Solvent-free Hydrogenation at 450°C, 1 hr, 70 bar (1015 psi) H₂ (cold)

(Weller and Pelipetz (1951)²⁴³ study as reported in ref. 1)

Catalyst	Mode of catalyst addition	Liquefaction yield, % maf coal			
		Conversion (benzene-solubles)	Asphaltene (hexane-insolubles)	Oil (by difference)	Gas
None	--	33.4	2.8	21.6	9.0
FeSO ₄ (1% Fe)	Powder Impregnated	38.9 84.9	6.9 38.9	18.9 31.0	13.1 15.0
NiCl ₂ (1% Ni)	Powder Impregnated	44.2 88.3	6.8 15.5	24.0 54.8	13.4 18.0
SnCl ₂ (1% Sn)	Powder Impregnated	82.3 88.3	26.5 19.9	41.3 52.9	14.5 15.5
NH ₄ molybdate	Powder Impregnated	33.7 92.7	1.0 27.2	24.6 51.9	8.1 13.6
+H ₂ SO ₄	Impregnated	94.7	10.0	70.8	13.9

Table 4a. Chemical Forms of Some Dispersed Catalysts
(Based on catalyst characterization after liquefaction)

Active Metal(s)	Catalyst Precursor	Sulfidation	Catalyst Form(s) Detected	Comments	Refs.
Sn	SnO ₂ powder	No	Liquid Sn	Molten tin dispersed in coal	31
	SnO ₂ aerosol	Presulfiding or in-situ (elemental S)	SnS + Fe _{1-x} S + some FeSn ₂	Presulfidation gave more SnS; Fe _{1-x} S from coal (French Freyming; FeSn ₂ from reaction of Sn with coal pyrite	32
	Sn metal	No	SnS + some FeSn ₂		
	SnO ₂ from hydrolysis of SnCl ₂	In-situ (H ₂ S)	Liquid Sn + SnS	Morwell and Gelliondale (Australian) coals	30
Mo	NH ₄ molybdate	Presulfiding H ₂ S	non-stoichiometric MoS ₂	S/Mo = 2.5 with H ₂ , 2.7 with N ₂ (h ₂ C coal)	34
Ni	Ni acetate	No	Ni metal	230-270°C with phenolics as solvents (Morwell)	130
				310-350°C with tetralin (Morwell, Wandoan, Akabira, Liddell)	130a
Ru	Ru ₃ (CO) ₁₂	No	RuS ₂ + Ru metal	400-425°C, Illinois No. 6 (high-S)	33
Co, Mo	Co-Mo thiosalt	--	MoS ₂ , Co ₉ S ₈ , and mixed Co-Mo sulfide	Catalyst prepared from thiosalt decomposition	202
Fe, Sn	FeSO ₄ /SnCl ₂	No	Fe, FeS, Sn, SnS, FeSn ₂	Morwell, >380°C: with Sn/Fe = 0.073	238
			FeS, Sn, SnS, SnS ₂ , FeSn ₂	with Sn/Fe > 1.7	

Table 4b. Active Forms of Dispersed Fe Catalysts
(Based on catalyst characterization after liquefaction)

Catalyst Precursor	Sulfidation	Catalyst Active Form	Comments	Refs.
Coal pyrite (FeS_2)	In-situ (H_2S)	Fe_{1-x}S	Morwell and Gelliondale (Australian) coals	30
	No		Illinois No. 6 (high-S)	197
FeS_2 or Fe_2O_3	In-situ (elemental S)	Fe_{1-x}S	Model compound study (active carbon to simulate coal)	229
Fe_2O_3 aerosols	In-situ (elemental S)	Fe_{1-x}S	Freyrming French coal; $1-x = 0.87, 0.90$	81
Fe_2O_3 powder	Yes (DMDS)	Fe_7S_8	catalyst generated from fine powder sulfided at 380°C	232
$\text{Fe}(\text{CO})_5$	No	Fe_{1-x}S (mostly) + Fe_3C + other Fe compounds	Illinois No. 6 in Maya atmospheric resid; 12 nm pyrrhotite	95
	No	Fe metal + cementite	Model compound study	229
	In-situ (elemental S)	Pyrrhotite	Mossbauer spectra of Fe_{1-x}S has an unidentified doublet peak	
Fe_2O_3 powders or $\text{Fe}_3(\text{CO})_{12}$	No	FeS	if coal $\text{Fe/S} = 3$	138
		Fe_{1-x}S	if coal $\text{Fe/S} = 0.3$	
Ferric naphthenate	Yes (DMDS)	$\text{FeS}_2, \text{FeS}, \text{Fe}_7\text{S}_8$	Simulated coal liquefaction conditions	232
$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	No	$\alpha\text{-Fe}, \gamma\text{-Fe}, \text{Fe}_3\text{C}$	Loy Yang coal; distribution of catalyst forms depends on iron loading	228
Sulfated Fe_2O_3	No	Fe_{1-x}S	Size of pyrrhotite from this precursor < that from coal pyrite	238

Table 5. Production of Catalyst Fine Powders

Method	Chemical Form	Examples	References
PRECIPITATION	Oxides	Fe ₂ O ₃	125, 180, 181, 194-196
		Fe ₃ O ₄	125, 180, 181
		SnO ₂	31, 194, 196
		MoO ₃ , V ₂ O ₅	US Patents 45-48
		CrO ₃	US Patents 132-134
	Oxyhydroxides	FeOOH	195
		SnO(OH) ₂	28
	Sulfides	MoS ₂ , MoS ₃	121, 140; 123, 142, 211
		Cr ₂ S ₃ , WS ₂ , RuS ₂ , FeS _x , MoS ₂	55, 86
	Nitrides & carbides	Transition metal	53, 54 (HDN of coal liquids)
MICROEMULSION-BASED TECHNIQUES	Others: Oxysulfides, borides, phosphides, metals		
	Oxides	Fe ₂ O ₃	74
	Sulfides	MoS ₂	76, 77
	Titanates	TiO ₂ w/ 0.7% Pd	70, 71
	Metals	Transition metals	61-64 (ceramic applications)
	Alloys		65, 66 (ceramic applications)
	Others: Carbonates, ferrites, selenides, phosphates		
	Metal salts		58 (general reference)
	Metals, oxides, sulfides	Fe ₂ O ₃ , SnO ₂ , MoO ₃	32, 80, 81, 87
	Carbides, sulfides, oxides	Fe ₃ C, Fe ₇ C ₃	84, 85, 141
SURFACE DEPOSITION (Incipient wetness)			
FLAME DECOMPOSITION			
LASER PHOTOLYSIS/ PYROLYSIS			

Table 6a. Oil-Soluble Catalyst Precursors

COMPOUNDS	EXAMPLES	REFERENCES
NAPHTHENATES	Mo	90, 185, 186 (model cpds.); 91 (coprocessing), 140 (>MoS ₂), 152 (with ultrasound)
	V	91 (coprocessing)
	Ni	92 (model cpds.), 91 (coprocessing)
	Cr	US Patents 116, 132-134
OCTOATES	Mo, Ni, V	91 (coprocessing)
	Ni	92 (model compounds)
CARBONYLS	Fe(CO) ₅	94 (Japanese coals), 95 (coprocessing), 141 (Wyodak subbitum.), 187 (Yallourn Australian), 143 (with preswelling); Japanese Patent 93 (high activity at 300°C)
	Fe ₃ (CO) ₁₂	138
	Mo(CO) ₆	99 (impregnation with supercritical CO ₂), 143 (with preswelling); 152 (with ultrasound)
	Fe(CO) ₅ + Mo(CO) ₆	112, 113 (coprocessing; Fe+Mo > Mo > Fe)
ORGANIC ACIDS	Ru ₃ (CO) ₁₂	33 [> Fe(CO) ₅], 98 (model compounds)
	Molybdic acid	4 (with ZnO/magnesia or chromic acid); US Patent 100
	Phosphomolybdic acid	US Patents 101, 102, 103 (with hydrogen halide), 104 (sulfiding unnecessary)
	Sulfonic acids	French Patent 114 (Fe(OH) ₃ + 10- to 35-C alkylbenzene)

Table 6a. Oil-Soluble Catalyst Precursors
(Continued)

COMPOUNDS	EXAMPLES	REFERENCES
ORGANIC SULFUR COMPOUNDS	Benzenethiol	111
	Thiol, thiophenol benzothiophene, alkyl mercaptans	European Patents 112, 113
OTHER ORGANOMETALLICS	Molyvan additives	106, 107
	Citrate	92 (Ni)
	Acetylacetonates	91 (Mo, Ni, V); 92 (Ni); 106 (Fe); 56 (Ru)
	Others	110 (Co phthalocyanine), 187 (ferrocene); 108 (tetraethyl lead, tetramethyl tin); 33 (Ru[cyclooctadiene][cyclooctatriene]); 94 ([Fe(CO) ₂ Cp] ₂ , Cp=cyclopentadienyl); Jap. Patent 115 (Mo[t-C ₄ H ₉ S] ₄)

Table 6b. Water-Soluble Catalyst Precursors

COMPOUNDS	EXAMPLES	REFERENCES
MOLYBDATES	NH ₄ tetrathiomolybdate (ATM)	117-119, 122, 123 ; 36, 211 (coprocessing); 121, 188 (with high-S coals); 124 (impregnation with THF/H ₂ O); 142 (with preswelling); 146 (with prehydrogenation); 208 (with mild vacuum drying pretreatment)
	NH ₄ molybdate (AM)	34, 118
	NH ₄ heptamolybdate (AHM)	122, 123; 120 (no donor solvent); 36 (coprocessing); 121 (with high-S coals)
	Tetrahydroquinolium molybdate	118
SULFATES	FeSO ₄	94 (Jap. coals); 125 (model cpds.); 176 (coprocessing); 136, 137, 143 (with preswelling)
	(NH ₄) ₂ SO ₄	125 (model cpds.); 126 (Jap. coals)
	CoSO ₄ 8H ₂ O	109 (only slightly better than thermal)
	Sulfated Fe and Sn oxides	194-196; 126, 198 (Fe, Jap. and Australian coals); 96, 97 (coprocessing)

Table 6b. Water-Soluble Catalyst Precursors
(Continued)

COMPOUNDS	EXAMPLES	REFERENCES
HALIDES	Metal chlorides	127 ($\text{FeCl}_2 < \text{ZnCl}_2 < \text{NiCl}_2 < \text{CuCl}_2 < \text{SnCl}_2 < \text{CoCl}_2$)
	FeCl_3	94 (Jap. coals); US Patents 103, 129
	ZnCl_2	144 (with methanol for swelling); US Patents 103, 129
	SnCl_2	144 methanol for swelling); 189 (Victorian coals)
	FeBr_2	149 (with organic production pretreatments)
	Hydrogen halides	148 (HCl with mild alkylation); US Patent 128
ACETATES	Ni	130 (with phenolics as liquefaction solvent)
	Fe	189 (Victorian coals)
	Pb	108 (Milmerran Australian coal)
OTHERS	Oxalates	US Patent 37 (V and Mo)
	Nitrates	228 ($\text{Fe}[\text{NO}_3]_3 \cdot 9\text{H}_2\text{O}$)

Table 7. Examples of Multicomponent Catalysts

Components	Form and concentration of components	References
Fe, Mo	1% Fe as $\text{Fe}_2(\text{SO}_4)_3$ 0.2% Mo as ammonia paramolybdate	14
	1% Fe as FeSO_4 0.02% Mo as NH_4 molybdate	234
	Fe as iron oxide aerosols	27, 32, 235
	<0.7 wt% Fe as sulfated Fe_2O_3 20-100 ppm Mo (as AHM and ATM) on coal	96, 195, 196
	Mo as AHM or ATM; 1% Fe + 0.1% Mo ~ 1% Mo >> 1% Fe (in terms of conv.)	237
	Fe as sulfated and non-sulfated Fe_2O_3 or FeOOH ; Mo as molybdate	28
	Fe as ion-exchanged; Mo as soluble precursor	137
	Fe and Mo as ores	8
	Fe and Mo as metals or sulfides; Mo could be replaced by Co, Ni, W, Ti, Sn, Zn, V, Cr, or Sb)	Japanese Patents 236a,b,c
	Mo could be replaced by Ni, Mn, Cr, W, Ti, Al, and Sn; 0.03-3 wt% P added	German Patent 233
Fe, Sn	Fe as FeOOH or Fe_2O_3 or FeOOH ; Sn as $\text{SnO}(\text{OH})_2$ or SnO_2 ; oxides may be sulfated	28
	Fe and Sn from flame decomposition of FeCl_3 and SnCl_4	80
	Fe from FeSO_4 ; Sn from SnCl_2	238
	Fe dissolved in HCl solution containing Sn halides	German Patent 239

Table 7. Examples of Multicomponent Catalysts
(Continued)

Components	Form and concentration of components	References
Fe, Mn	Fe and Mn as mixed oxides, hydroxides, or sulfates (0.2-5 wt% based on feed)	25
	Fe and Mn as ores	8
Fe, Ru	Fe as FeS ₂ ; Ru as RuCl ₃	241
Mo, Ru, P	Mo-P/RuCl ₃ -H ₂ O (high activity for quinoline hydrogenation)	213
Mo, Halide	Halide as hydrogen halide	US Patent 103
Cu, Mo (or W, Co, Ni)	5000-15,000 ppm as CuSO ₄ ; 100-1000 ppm NH ₄ molybdate	US Patent 241
Zn, Mo (or W, Co, Ni)	5000-15,000 ppm Zn as ZnSO ₄ , ZnCl ₂ , nitrate, oxalate, acetate, bromide, octoate, or naphthenate; 100-1000 ppm Mo as NH ₄ molybdate or phosphomolybdic acid	US Patent 241
Cu, Al (or Mg, Ni, Zn, Cr)	10-70% Cu; 1-30% Al (or Mg, Ni, Zn, Cr); catalyst 0.2-5 wt% of feed	US Patent 241
Mo, P and one of Co, Ni, Fe, V, Ti, Zn, Cu, or W)	Mo as soluble complex; 10-1000 ppm of co-catalyst	Japanese Patent 212
Fe, Mo, Co	Fe, Mo, Co as ores	8
Mo, Ni, Al	Mo, Ni, Al as ores	8

Table 8. Crystalline Phases in the Fe-S System
[From Srinivasan, et. al. (1992)²³²]

Formula	Crystal Structure	Lattice Parameters, Å		
		a	b	c
FeS ₂	Cubic	5.417	--	--
FeS ₂	Orthorhombic	4.436	5.414	3.381
FeS	Cubic	5.423	--	--
FeS	HCP ⁽¹⁾	5.967	--	11.735
FeS	Tetragonal	3.676	--	5.032
Fe _{1-x} S	HCP ⁽¹⁾	6.88	--	22.90
β -Fe _{1-x} S	HCP ⁽¹⁾	6.894	--	40.15
Fe ₉ S ₈	Tetragonal	3.679	--	5.047
Fe ₇ S ₈	HCP ⁽¹⁾	6.867	--	17.062
Fe ₇ S ₈	Monoclinic	11.902	6.859	22.787
Fe ₃ S ₄	HCP ⁽¹⁾	3.47	--	34.5
Fe ₃ S ₄	Cubic	9.876	--	--

⁽¹⁾ HCP = hexagonal close packed

REFERENCES:

1. Derbyshire, F. J. "Catalysis in Coal Liquefaction: New Directions for Research", IEACR/08, IEA Coal Research, London, June 1988.
2. Charcosset, H.; Genard, A. "Catalysis in Direct Coal Liquefaction", EUR11191, Comm. Eur. Communities, Synth. Fuels Coal, 1987, pp. 339-381.
3. Narain, N. K.; Cillo, D. L.; Stiefel, G. J.; Tischer, R. E. "Disposable Catalysts in Coal Liquefaction", in Volborth, A. (ed.) Coal Science and Chemistry, Amsterdam: Elsevier Science Publishers, 1987, pp. 111-149.
4. Donath, E. E. "History of Catalysis in Coal Liquefaction", in Anderson, J. R.; Boudart, M. (eds.) Catalysis Science and Technology, New York: Springer-Verlag, 1982, pp. 1-38.
5. Lee, J. M.; Cantrell, C. E. "Effect of Coal Rank and Quality on Two-Stage Liquefaction" Fuel Proc. Tech., 1991, 29, 171-197.
6. Chiyoda Chemical Engineering Company, "Liquefaction of Coal by Hydrogenation" Japanese Patent J56072079, 6/16/81.
7. Ikura, M.; Kelly, J. F. "Two-stage Coprocessing of Coal and Heavy Hydrocarbon, e.g., Bitumen" Canadian Patent 1279027, 1/15/90.
8. Mathur, V. K.; Fackoukakis, E. P.; Ruether, J. A. "Coal Liquefaction Using Ore Catalysts" Fuel, 1984, 62, 1700-1705.
9. Mathur, V. K.; Reddy Karri, S. B. "Ore Catalysts in Two-Stage Coal Liquefaction" Fuel, 1986, 65, 790-796.
10. Tsao, Y. Y. P. "Selective Hydrogenation of Polynuclear Aromatic Compounds" US Patent 4696733, 9/29/87.
11. Varghese, P. "Coal Liquefaction Using Manganese Nodules as Catalyst" US Patent 4610777, 9/9/86.
12. Mitchell, T. O.; Whitehurst, D. D.; Farcasiu, M. "Desulphurising, Demetallising, and Denitrogenating Coal" US Patent 4303497, 12/1/81.
13. Mitsui Coke Kogyo, "Coal Liquefaction" US Patent 4354919, 10/19/82.
14. Batenin, V. M.; Lipovich, V. G. "New Catalysts to Promote Coal Liquefaction" in International Conference on Coal Science Proceedings 1991 - IEA Coal Research, Oxford: Butterworth-Heinemann Ltd., 1991.

15. Veb Otto Grotewohl, "Hydrogenation of Lignite" German Patent 265415, 1/31/89.
16. Veba Leuna-Werk Ulbricht, "Semi-solid Phase Catalyst Production for Coal Hydrogenation" German Patent 274984, 1/10/90.
17. Veb Otto Grotewohl, "Sump Phase Hydrogenation of Coal or Heavy Oil" German Patent 275252, 1/17/90.
18. Veb Otto Grotewohl, "High Pressure Hydrogenation of Coal or Heavy Oil" German Patent 275253, 1/17/90.
19. Wallach, D.; Zimmermann, G.; Anders, K.; Sommer, H.; Kunze, P.; Becker, K.; John, H. "Converting Residue from Petroleum Processing and Coal Liquefaction" German Patent 270314, 7/26/89.
20. Wallach, D.; Zimmermann, G.; Anders, K.; Sommer, H.; Kunze, P.; Becker, K.; John, H. "Converting High Boiling Hydrocarbon Feed in Reactive Solvent" German Patent 270312, 7/26/89.
21. John, H.; Becker, K.; Berrouscho, H. D.; Sommer, H.; Kubze, P.; Ktrumsdorf, T. "Sump Phase Catalyst for Hydrogenating Coal" German Patent 279420, 3/14/91.
22. Mitsubishi Chemical Industries; Kobe Steel; Idemitsu Kosan; Asia Sekiku "Coal Liquefying Process with Reduced Catalyst Loss" Japanese Patent 58171478, 10/8/83.
23. Wernicke, H. J.; Zimmermann, H. "Blast Furnace Flue Dust as Coal Hydrogenation Catalyst" US Patent 4515678, 5/7/85.
24. Schlutter, E.; Sommer, H. "Hydrogenating Coal or Heavy Oil on Catalyst" German Patent 285510, 12/19/90.
25. Wallach, D.; Zimmermann, G.; Anders, K.; Sommer, H.; Kunze, P. "Hydrocarbon-Containing Residue Reprocessing" German Patent 282024, 8/29/90.
26. Sato, Y.; Minami, R.; et. al. "Effects of Iron Catalysts on the Composition of Oil from Coal Liquefaction" *Fuel Sci. Technol. Int.* 1987, 5, 357-371.
27. Bacaud, R.; Charcosset, H.; Jamond, M. "Determination of Coal Reactivity in Catalyzed Hydroliquefaction" *Fuel Proc. Technol.* 1990, 24, 163-169.
28. Reucroft, P. J.; Kim, J. Y. "XPS Study of Catalysts and Catalyst Impregnated Coal" ACS 203rd National Meeting, ACS Div. Fuel Chem. Preprints, 37 #2:756-63, 1992.
29. Buchanan, A. C. III; Britt, P. F.; Biggs, C. A. "Dispersed Catalysts: Evidence for a Role for Solid-State Interactions" *Energy & Fuels*, 1992, 6, 110-112.

30. Rogers, D. E.; Agnew, J. B. "Some Aspects of the Behaviour of Inorganic Constituents of Two Australian Brown Coals During Hydroliquefaction" *Fuel*, 1981, 60, 914-918.
31. Mizumoto, M.; Yamashita, H.; Matsuda, S. "Hydroliquefaction of Coal with Tin Oxide Catalyst" *Ind. Eng. Chem. Prod. Res. Dev.* 1985, 24, 394-397.
32. Besson, M.; Bacaud, R.; Brodski, D.; Bussiere, P.; Charcosset, H.; Djega-Mariadassou, G.; Oberson, M.; Sharma, B. K. "Hydroliquefaction of Coal Catalyzed by Tin Compounds" *Fuel*, 1990, 69, 35-43.
33. Suzuki, T.; Yamada, H.; Yunoki, K.; Yamaguchi, H. "Highly Active Coal Liquefaction Catalyst: Soluble Ruthenium Complexes as Catalyst Precursors" *Energy & Fuels*, 1992, 6, 352-356.
34. Mitchell, G. D.; Davis, A.; Derbyshire, F. J. "Microscopic Observations of Dispersed Liquefaction Catalysts" in International Conference on Coal Science Proceedings 1991 - IEA Coal Research, Oxford: Butterworth-Heinemann Ltd., 1991.
- 34a. Cugini, A. V.; Utz, B. R.; Krastman, D.; Hickey, R. F.; Balsone, V. "Effect of Activation Conditions on Dispersed Hydrated Iron Oxide Catalyst Precursors" Second Annual Joint DOE/DEMRC Technical Workshop on Coprocessing, Atlanta, GA, June 11-12, 1991.
35. Krastman, B.; Utz, R.; et. al. "Dispersed-phase Molybdenum Catalyst Recovery in Coprocessing" 198th ACS National Meeting, Boston, MA, ACS Div. Fuel Chem. Preprints, 35 #2:570-576, 1990.
36. Cugini, A. V.; Lett, R. G. "Coal/Oil Coprocessing Mechanism Studies" 195th ACS National Meeting, Toronto, ACS Div. Fuel Chem. Preprints, 33 #1:77-88, 1988.
37. Bearden, R.; Aldridge, C. L. "Slurry Hydroconversion Process Uses Vanadyl Oxalate Catalyst Precursor" US Patent 4548700, 10/22/85.
38. Singhal, G. H.; Nadkarni, R. A. "Catalyst Recovery in Coal Liquefaction" US Patent 4434043, 2/28/84.
39. Cugini, A. V.; Balsone, V.; et. al. "Novel Dispersed-phase Catalytic Approach to Coprocessing" 195th ACS National Meeting, Toronto, ACS Div. Fuel Chem. Preprints, 33 #1:6-19, 1988.
40. Srivastava, R. D.; Baird, M. J. "Catalysis in Direct Liquefaction of Coal", ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:124-32, 1992.
41. Gatsis, J. G. "Coal Liquefaction Process" US Patent 4294248, 7/19/83.

42. Gatsis, J. G. "Hydrocarbon Production from Coal" US Patent 4431510, 2/14/84.
43. Gatsis, J. G. "Process for Liquefying Coal" US Patent 4394248, 7/19/83.
44. Gatsis, J. G. "Method of Solvent Extraction of Coal by a Heavy Oil" US Patent 4338183, 7/6/82.
45. Gatsis, J. G. "Process Utilizing a Non-Stoichiometric Vanadium Sulfide Catalyst in Hydrocarbon Hydrorefining" US Patent 4197191, 4/8/80.
46. Gatsis, J. G. "Hydrocarbon Hydrorefining Process Utilizing a Non-Stoichiometric Vanadium Sulfide Catalyst" US Patent 4194967, 3/25/80.
47. Gatsis, J. G. "Process for Hydrorefining a Hydrocarbon Utilizing a Non-Stoichiometric Vanadium Sulfide Catalyst" US Patent 4199439, 4/22/80.
48. Gatsis, J. G. "Method of Catalyst Preparation" US Patent 4303634, 12/1/81.
49. Gatsis, J. G. "Single-Stage Slurry Catalyzed Coprocessing Developments" ACS 200th National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 1990, 35: #4:975-987.
50. Gatsis, J. G.; Roemisch, R. W.; Miller, M. A.; Piasecki, C. A.; Fullerton, H. E. "High-severity Coprocessing" ACS 203rd National Meeting, ACS Div. Fuel Chem. Preprints, 37 #1:160-171, 1992.
51. Nafis, D. A.; Humbach, M. J.; Gatsis, J. G. "Coal Liquefaction Coprocessing: Final Report" DOE/PC/70002-T6, September 1988.
52. Lopez, J.; McKinney, J. D.; Pasek, E. A. "Heavy Oil Hydroprocessing" US Patent 4557821, 12/10/85.
53. Liu, Z.; Griswold, S.; Dadyburjor, D. B. "Design of Group III Nitrides as Novel Catalysts for HDN of Model Coal-Liquid Compounds" Chem. Eng. Sci. 1992, 47, 2722-2732.
54. Oyama, S. T. "Preparation and Catalyst Properties of Transition Metal Carbides and Nitrides" Cat. Today 6/30/92, 15(2), 179-200.
55. Chianelli, R. R.; Pecoraro, T. A.; Dines, M. B. "Hydrotreatment of Petroleum or Coal-Derived Hydrocarbons" US Patent 4368115, 1/11/83.
56. Che, M.; Bonneviot, L. "The Change of Properties of Transition Metal Ions and the Role of the Support as a Function of Catalyst Preparation" in Successful Design of Catalysts Inui, T. (ed.), 1988: Elsevier Science Publishers B. V., Amsterdam, pp. 147-158.

57. Aries, L.; Traverse, J. P. "Preparation of Supported Microporous Catalyst Useful in Hydrogenation" World Patent 8804576, 6/30/88.
58. Cusumano, J. A.; Dalla Betta, R. A.; Levy, R. B. "Scientific Resources Relevant to the Catalytic Problems in the Conversion of Coal" Final Report of ERDA Contract No. E(49-18)-2017, NTIS FE-2017-1, October 1976.
59. Agency of Industrial Science and Technology, "Coal and Bituminous Material Coliquefaction" Japanese Patent 03243691, 10/30/91.
60. Matijevic, E. "Monodispersed Inorganic Colloids Have Become Reality" *J. Mater. Educ.* 1988, 10, 177-204.
61. Bonnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Joussen, T.; Korall, B. "Formation of Colloidal Transition Metals in Organic Phases and their Application in Catalysis" *Angew. Chem. Int. Ed. Engl.* 1991, 30, 1312-1324.
62. Boutonnet, M.; Kizling, J.; Stenius, P. "The Preparation of Monodisperse Colloidal Metal Particles from Microemulsions" *Colloids and Surfaces* 1982, 5, 209-225.
63. Suslick, K. S.; Choe, S.-K.; Cichowlas, A. A.; Grinstaff, M. W. "Sonochemical Synthesis of Amorphous Iron" *Nature* 1991, 353, 414-416.
64. Glavee, G. N.; Klabunde, K. J.; Sorensen, C. M.; Hadjapanayis, G. C. "Borohydride Reductions of Metal Ions. A New Understanding of the Chemistry Leading to Nanoscale Particles of Metals, Borides, and Metal Borates" *Langmuir* 1992, 8, 771-773.
65. Bonnemann, H.; Brijoux, W.; Joussen, T. "The Preparation of Finely Divided Metal and Alloy Powders" *Angew. Chem. Int. Ed. Engl.* 1990, 29, 273-275.
66. Gassner, W.; Rossner, W.; Tomandl, G. "Synthesis of Yttria-Gadolinia Powders with Spherical Particle Morphology by Emulsion Technique" in *Ceramics Today -- Tomorrow's Ceramics, Part B* ed. P. Vincenzini, Amsterdam: Elsevier Science Publishers, 1991, pp. 951-958.
67. Reynen, P.; Bastius, H.; Fiedler, M. "The Use of Emulsions in the Preparation of Ceramic Powders" in *Ceramic Powders* ed. P. Vincenzini, 1983, Amsterdam: Elsevier Scientific Publishing Company, 1983, pp. 499-504.
68. Itoh, H.; Nagano, S.; Urata, T.; Kikuchi, E. "Liquid-Phase Fischer-Tropsch Synthesis on Manganese-Promoted Ultrafine Particles of Iron Used as a Catalyst" *Applied Catalysis*, 1991, 77, 37-43.

69. Kikuchi, E.; Itoh, H. "Liquid Phase Fischer-Tropsch Synthesis on Iron Ultrafine Particle Catalysts" *Sekiyu Gakkaishi* 1991, 34, 407-415.
70. Johnston, K. P.; Lynch, A. W.; Padrick, T. D.; Stephens, H. P.; Stohl, F. V. "Coal Liquefaction Process Research" DOE Quarterly Report, July 1 - September 30, 1982.
71. Snape, C. E.; Dosch, R. G.; Bolton, C.; Stephens, H. P. "High-Liquid Yields from Bituminous Coal via Hydropyrolysis with Dispersed Catalyst" ACS 196th National Meeting, Los Angeles, CA, ACS Div. Fuel Chem. Preprints, 33 #3:351-356, 1988.
72. Wilcoxon, J.; Martino, A.; Nigrey, P.; Sylwester, E.; Klavetter, E.; Baughman, R. "Formation and Characterization of Highly-Dispersed Metal Colloid Catalysts" Proc. Eight Annual International Pittsburgh Coal Conf. 1991, 703.
73. Wilcoxon, J. P.; Sylwester, A.; Nigrey, P.; Martino, A.; Quintana, C.; Baughman, R. J. "Formation and Characterization of Highly-Dispersed Iron Catalysts" Proc. Liquefaction Contractors Review Meeting 1991, 411.
74. Linehan, J. C.; Bean, R. M.; et. al. "New Synthetic Methods for the Production of Ultra-fine Coal Liquefaction Catalysts" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:488-496, 1992.
75. Stiller, A.; Zondlo, J.; Dadyburjor, D.; Stansberry, P. "Studies of Fe₂S₃ as a Precursor for the Iron Sulfide Mineral Series" Presented at the Fourth Annual Technical Meeting of the Consortium for Fossil Fuel Liquefaction Science, Snow Bird, UT, August 1990.
76. Boakye, E.; Vaidyanathan, N.; et. al. "Microemulsion-mediated Synthesis of Nanosize Molybdenum Sulfide Coal Liquefaction Catalysts" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:298-305, 1992.
77. Vaidyanathan, N.; Boakye, E.; et. al. "Liquefaction of a Subbituminous Coal in the Presence of Novel Microemulsion-based Molybdenum Catalysts" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:480-487, 1992.
78. Smith, G. D.; Donelan, C. E.; Barden, R. E. "Oil Continuous Microemulsions Composed of Hexane, Water, and 2-Propanol" *J. Colloid Interface Sci.* 1977, 60(3), 488-496.
79. Milburn, D. R.; Adkins, B. D.; Davis, B. H. "Preparation of a Colloidal Hydrotreating Catalyst", *Symp. on New Catalytic Materials and Techniques*, ACS Division of Petroleum Chemistry, Miami Beach Meeting, Sept. 10-15, 1989.

80. Pregermain, H.; Charcosset, ; Andres, M. "More Active Coal Hydrogenation Catalyst" US Patent 4510039, 4/9/85.
81. Djega-Mariadassou, G.; Besson, M.; Brodzki, D.; Charcosset, H.; Huu, T. V.; Varloud, J. "Evolution of Highly Dispersed Catalysts During Hydroliquefaction of Coal" *Fuel Proc. Tech.* 1986, vol. 12, pp. 143-153.
82. Kriechbaum, G. W.; Kleinschmit, P. "Superfine Oxide Powders - Flame Hydrolysis and Hydrothermal Synthesis" *Angew. Chem. Int. Ed. Engl. Adv. Mater.* 1989, 28, 1416-1423.
83. Grazis, B. M. ed. *Surveys of Research in the Chemistry Division*, Argonne National Laboratory, 1991.
84. Eklund, P. C.; Stencel, J. M.; Bi, X. X.; Keogh, R. A.; Derbyshire, F. J. "Ultrafine Iron Catalyst for Coal Dissolution" ACS 201st National Meeting, Atlanta, GA, ACS Div. Fuel Chem. Preprints, 36 #2:551-560, 1991.
85. Eklund, P. C.; Bi, X. X.; Derbyshire, F. J. "Nanoscale Fe-Based Catalysts from Laser Pyrolysis" ACS 204th National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 37 #4:1781-1792, 1992.
86. Tarrer, A. R.; Guin, J. A.; Tatarchuk, B. J.; Curtis, C. W. "New and Improved Dispersion and Recovery Techniques for Slurry Phase Catalysis" DOE Final Technical Report, DOE/PC/60044--T8, January 1988.
87. Tekely, B.; Bacaud, R.; Kister, J.; Charcosset, H.; Delpuech, J. J.; Nicole, D.; Oberson, M. "Structural Changes of Highly-volatile Bituminous coal After Catalytic Hydrogenation at 350°C, as Revealed by ¹³C CP/MAS NMR and FT-IR" *Fuel*, 1988, 67, 932-937.
88. Hirschon, A. S.; Wilson, R. B. "Use of Dispersed Catalysts for Coal Liquefaction" ACS 198th National Meeting, Miami Beach, FL, ACS Div. Fuel Chem. Preprints, 34 #3:881-886, 1989.
89. Hirschon, A. S.; Wilson, R. B. "Designed Coal Liquefaction Catalysts" ACS 201st National Meeting, Atlanta, GA, ACS Div. Fuel Chem. Preprints, 36 #1:103-107, 1992.
90. Curtis, C. W.; Pellegrino, J. L. "Activity and Selectivity of Mo Catalysts in Coal Liquefaction Reactions" 195th ACS National Meeting, Toronto, ACS Div. Fuel Chem. Preprints, 33 #1:376-383, 1988.
91. Kim, H.; Curtis, C. W. "The Catalytic Activity of Organometallic Complexes in Coprocessing" 200th ACS National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 35 #4:1064-1070, 1990.

92. Kim H.; Curtis, C. W. "Evaluation of the Activity of Nickel in Coprocessing using Model Systems" *Fuel Sci. Tech. Int.* 1991, 9, 229-252.
93. Takegami, Y. "Coal Liquefaction Process" Japanese Patent 58167681, 10/3/83.
94. Watanabe, Y.; Yamada, O.; Fujita, K.; Takegami, Y.; Suzuki, T. "Coal Liquefaction Using Iron Complexes as Catalysts" *Fuel*, 1984, 63, 752-755.
95. Herrick, D. E.; Huffman, G. P.; Tierney, J. W.; Wender, I.; Huggins, F. E. "Activity and Characterization of Coprocessing Catalysts Produced from an Iron Pentacarbonyl Precursor" *Energy & Fuels*, 1990, 4, 231-236.
96. Pradhan, V.; Tierney, J. W.; Wender, I. "Sulfated Metal Oxides as Catalysts for Coal-Oil Coprocessing" ACS 201st National Meeting, Atlanta, GA, ACS Div. Fuel Chem. Preprints 36 #2:597-604, 1991.
97. Pradhan, V. R.; Herrick, D. E.; et. al. "Finely Dispersed Iron, Iron-Molybdenum, and Sulfated Iron Oxides as Catalysts for Coprocessing Reactions" *Energy & Fuels*, 1991, 5, 712-20.
98. Hirschon, A. S.; Laine, R. M.; Wilson, R. B. Jr.; Ackerman, L. L. "Catalytic Methods for Improved Coal Liquefaction and Hydrotreating" DOE Final Report, DOE/PC/80906--9, March 1988.
99. Warzinski, R. P.; Lee, C. H.; Holder, G. D. "Supercritical-fluid Solubilization of Catalyst Precursors: The Solubility and Phase Behavior of Molybdenum Hexacarbonyl in Supercritical Carbon Dioxide and Application to the Direct Liquefaction of Coal" *J. Supercrit. Fluids*, 1992, 5(1), 60-71.
100. Bearden, R.; Aldridge, C. L.; Lewis, W. E.; Mayer, F. X.; Taylor, J. H. "Preparation of Active Mo-Containing Hydroconversion Catalyst" European Patent 243143, 10/28/87.
101. Bearden, R.; Aldridge, C. L.; Mayer, F. X.; Taylor, J. H.; Lewis, W. E. "Slurry Hydroconversion of Carbonaceous Material", US Patent 4740295, 4/26/88.
102. Bearden, R.; Aldridge, C. L. "Molybdenum Preparation Containing Catalyst" US Patent 4637871, 1/20/87.
103. Bearden, R.; Baird, W. C.; Aldridge, C. L. "Hydroconversion of Oil or Coal" European Patent 93809, 11/16/83.
104. Aldridge, C. L.; Bearden, R. "Hydroconversion of Coal-Oil Mixtures" US Patent 4298454, 11/3/81.
105. Lewis, W. E.; Mayer, F. X. "Slurry Process for Hydroconverting Heavy Oils Using Catalyst" European Patent 243142, 10/28/87.

106. Swanson, A. J. "Dispersed Molybdenum Catalysts for Liquefaction of Illinois No. 6 Coal" ACS 203rd National Meeting, San Francisco, CA. ACS Div. Fuel Chem. Preprints, 37 #1:149-155, 1992.
107. Lee, J. M.; Vimalchand, P. et. al. "Performance of a Hybrid Catalyst System in Coal Liquefaction" ACS 204th National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 37 #4:1886-1894, 1992.
108. Attala, M. I.; Quezada, R. A.; et. al. "Tetraethyl Lead as a Coal Liquefaction Promoter" Fuel 1992, 4, 401-407.
109. Wilson, B. L.; Charles, A.; Jackson, K. "Soluble Cobalt(II) Complex as Catalyst for Direct Coal Liquefaction" Fuel, 1988, 67, 437-438.
110. Sakamoto, K.; Sonobe, J.; Shimizu, F.; Shibamiya, F. "The Hydrocracking of Khafji Asphaltene with Cobalt Phtalocyanine (Co-PhCy) Catalyst" Nippon Kagaku Kaishi, 1989, 7, 1111-1118.
111. Charcosset, H.; Dou, H. J. M.; Weller, S. W. "Fundamental Aspects of Liquefaction of Coal by Hydrogenation Under Pressure" Bull. Soc. Chim. Fr. 1986, 1, 6-9.
112. Rudnick, L. R. "Hydrogen Transfer from Alicyclic Donor to Acceptor" European Patent (EP) 195541, 9/24/86.
113. Rudnick, L. R. "Hydrogen Transfer from Long-Chain donor to Acceptor" European Patent (EP) 195539, 9/24/86.
114. Born, M.; Deschamps, A.; Frackowia, S.; Martino, G. "Catalytic Hydroliquefaction of Coal" French Patent 2486536, 1/15/82.
115. Japan Synthetic Rubber, Patent No. J57140791-A, Japan, 82.08.31, "Tetrakis (tert butyl thiolate) Molybdenum - Used for Preparation of Catalytic Molybdenum Complexes"
116. Exxon Research and Engineering Company "Coal Hydroconversion Process Using Dispersed Chromium-Containing Catalyst" US Patent 4793916, 12/27/88.
117. Li, B.; Braekman-Danheux, C.; Cypres, R. "Catalytic Hydropyrolysis of Bituminous Belgian Beringen Coal by Impregnated Sulphided Mo Catalyst" Fuel, 1991, 70, 254-258.
118. Burgess, C. E.; Artok, L.; Schobert, H. H. "Effect of Molybdenum Sulfide Catalyst on the Mechanism of Coal Liquefaction" ACS 201st National Meeting, Atlanta, GA, ACS Div. Fuel Chem. Preprints, 36 #2:462-469, 1991.
119. Davis, A.; Derbyshire, F. J.; Lin, R.; Mitchell, G. D.; Schobert, H. H. "Microscopic Evidence of Competing Hydrogenation and

- Condensation Reactions during Coal Liquefaction" ACS 201st National Meeting, ACS Div. Fuel Chem. Preprints, 36 #2:445-453, 1991.
120. Derbyshire, F. J.; Terrer, M-T.; Davis, A.; Lin, R. "Dry Catalytic Liquefaction of a Subbituminous Coal: Structural Inferences" *Fuel*, 1988, 67, 1029-1035.
 121. Garcia, A. B.; Schobert, H. H. "Comparative Performance of Impregnated Molybdenum-Sulphur Catalysts in Hydrogenation of Spanish Lignite" *Fuel* 1989, 68, 1613-1616.
 122. Bockrath, B. C.; Illig, E. G.; Keller, M. J. "Catalysis of Low Temperature Liquefaction by Molybdenum Sulfides" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:133-140, 1992.
 123. Utz, B. R.; Cugini, A. V.; Frommell, E. A. "Dispersed-Phase Catalysis in Coal Liquefaction" 198th ACS National Meeting, Miami Beach, FL, ACS Div. Fuel Chem. Preprints, 34: #4:1423-1430, 1990.
 124. Huang, L.; Song, C.; Schobert, H. H.; "Temperature-Programmed Catalytic Liquefaction of Low Rank Coal Using Dispersed Mo Catalyst" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:223-227, 1992.
 125. Yokoyama, S.; Yamamoto, M.; Maekawa, Y.; Kotanigawa, T. "The Catalytic Activity of Sulphate for Hydroliquefaction of Coal by Using Diphenylether and Diphenylmethane" *Fuel* 1989, 68, 531-533.
 126. Yokoyama, S.; Yamamoto, M.; Yoshida, R.; Maekawa, Y.; Kotanigawa, T. "Catalytic Behaviour of Sulphate and Sulphide in S-promoted Iron Oxide Catalysts for Liquefaction of Bituminous Coal and Lignite" *Fuel*, 1991, 70, 163-168.
 127. McCandless, F. P.; Waterman, J. J.; Sire, D. L. "Coal Hydrogenation and Hydrocracking Using a Metal Chloride/Gaseous HCl Catalyst System" *Ind. Eng. Chem. Proc. Des. Dev.*, 1981, 20, 91.
 128. Rhodes, R. P. "Liquefaction and Gasification of Carbonaceous Material" US Patent 443905, 3/27/84.
 129. Bearden, R.; Baird, W.; Aldridge, C. L. "Hydroconversion of Carbonaceous Feed, e.g., Coal Liquefaction" US Patent 4424110, 1/3/84.
 130. Takemura, Y.; Saito, Y. "Nickel-Catalyzed Hydroliquefaction of Morwell Brown Coal at Low Temperatures Using Phenolic Compounds as Solvents" *Energy & Fuels*, 1989, 3, 342-345.
 - 130a. Takemura, Y.; Okada, K. "Coal Hydroliquefaction Activity of Nickel Catalyst Using a Nickel Acetate Precursor" *Fuel*, 1988, 11, 1548-1553.

131. Ihara, H. "Coal Solvent Production by Hydrogenating Hydrocarbon Feed" US Patent 4495089, 1/22/85.
132. Bearden, R.; Aldridge, C. L. "Chromium-Containing Catalyst for Hydroconversion of Heavy Oil and Coal" US Patent 4579838, 4/1/86.
133. Bearden, R.; Aldridge, C. L. "Chromate Reaction Product Catalysts in Hydroconversion Processes" US Patent 457812, 3/25/86.
134. Bearden, R.; Aldridge, C. L. "Catalyst for Hydroconverting Carbonaceous Materials" US Patent 4567156, 1/28/86.
135. Edelson, E. H.; Stiefel, E. I.; Chianelli, R. R.; Coyle, C. L. "Hydroconversion of Solid Carbonaceous Materials" US Patent 4604183, 2/5/86.
136. Miki, K.; Yamamoto, Y.; Inaba, A.; Sato, Y. "Liquefaction of Subbituminous Coal in the Presence of Dispersed Iron and Molybdenum Catalysts" in International Conference on Coal Science Proceedings 1991 IEA Coal Research, Oxford: Butterworth-Heinemann Ltd., 1991.
137. Miki, K.; Yamamoto, Y.; Inaba, A.; Sato, Y. "Liquefaction of Iron-Loaded Subbituminous Coal in the Presence of a Sulphur source" Fuel, 1992, 71, 825-829.
138. Cook, P. S.; Cashion, J. D. "Mossbauer Study of Iron Catalysis in Victorian Brown Coal Liquefaction" Fuel, 1987, 66, 669-677.
139. Cook, P. S.; Cashion, J. D. "Mossbauer Study of Iron Exchanged Into Victorian Brown Coal" Fuel, 1987, 66, 661-668.
140. Curtis, C. W.; Pellegrino, J. L. "Activity and Selectivity of Three Molybdenum Catalysts for Coal Liquefaction Reactions", Energy & Fuels 1989, 3, 160-168.
141. Hager, G. T.; Bi, X. X.; Derbyshire, F. J.; Eklund, P. C.; Stencel, J. M. "Ultrafine Iron Carbide as Liquefaction Catalyst Precursor" ACS 202nd National Meeting, New York, NY, ACS Div. Fuel Chem. Preprints, 36 #4 1900-1908, 1991.
142. Artok, L.; Schobert, H. H.; Mitchell, G. D.; Davis, A. "Swelling Pretreatment of Coals for Improved Liquefaction" ACS 201st National Meeting, ACS Div. Fuel Chem. Preprints, 36 #1:36-43, 1992.
143. Davis, A.; Schobert, H. H.; Mitchell, G. D.; Artok, L. "Catalyst Dispersion and Activity Under Conditions of Temperature-Staged Liquefaction" Technical Progress Report, DOE, Jan. - Mar. 1991
144. Miura, K.; Mae, K. et. al. "Flash Hydropyrolysis of the Coal Supporting a Catalyst Through Solvent Swelling" ACS 204th National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 37 #4:1575-1582, 1992.

145. Joseph, J. T. "Carbonaceous Solid Pretreatment Before Liquefaction" World Patent 9112297, 8/22/91.
146. Bolton, C.; Derbyshire, F. J. "Effect of Low-Temperature Catalytic Hydrogenation on Pyrolysis and Hydropyrolysis of a Bituminous Coal" *Fuel*, 1988, 67, 901-905.
147. Derbyshire, F.; Davis, A.; Stansberry, R.; Schobert, H. "Low-temperature Catalytic Coal Hydrogenation: Pretreatment for Liquefaction" ACS 199th National Meeting, Boston, MA, ACS Div. Fuel Chem. Preprints, 35 #1:51-60, 1990.
148. Baldwin, R. M.; Miller, R. L. "Process and Analytical Studies of Enhanced Low Severity Coprocessing Using Selective Coal Pretreatment" DOE Quarterly Technical Report, December 1989-February 1990.
149. Nomura, M.; Fujimoto, T.; Miyake, M. "Hydroliquefaction of Subbituminous Coal. Effectiveness of Pretreatment by Organic Reduction with Sodium or Potassium" *Fuel*, 1985, 64, 1401-1404.
150. Ha, B. C.; Ruether, J. A.; Smith, D. N.; Mims, J. A. "Hydroliquefaction of Coal-Oil Agglomerates" ACS 196th National Meeting, ACS Div. Fuel Chem. Preprints, 33 #3:343-350, 1988.
151. Ruether, J. A.; Simpson, T. B. "Coal Hydrogenation" US Patent 5015366, 5/14/91.
152. Bendale, P. G.; Joseph, S.; Tierney, J. W.; Wender, I. "Use of Ultrasound for Enhanced Direct Coal Liquefaction: Final Report, August 1988 - November 1990", 1991, Report [D3REP3] 1990, DOE/PC/88816-T9.
153. Wambeke, A.; Toulhoat, H.; Boutrois, J. P.; Grimblot, J.; Bonnelle, J. P. "On the Addition of Various Metals as Inorganic Salts or Organometallic Complexes to a MoS_2 - $\gamma\text{Al}_2\text{O}_3$ Hydroprocessing Catalyst: Preparation, Characterization and Hydrogenation Activity" *Stud. Surf. Sci. Catal.*, 1987, 31, 581-589.
154. Bearden, R.; Aldridge, C. L. "Novel Catalyst and Process to Upgrade Heavy Oils" *Energy Prog.* 1981, 1, 44-48.
155. Aldridge, C. L.; Bearden, R. "Hydrocracking Hydrocarbon Oils" US Patent 4313818, 2/2/82.
156. Aldridge, C. L. "Catalytic Hydroliquefaction of Coal" European Patent 38171, 10/21/81.
157. Aldridge, C. L.; Bearden, R. "High Surface Area Catalysts" US Patent 4244839, 1/13/81.
158. Bearden, R.; Aldridge, C. L. "Heavy Oil Hydroconversion" US Patent 5039392, 8/13/91.

159. Singhal, G. H.; Wilson, B. L.; Edelson, M. A. "Hydroconversion of Carbonaceous Material, Especially Coal" Canadian Patent 1249536, 1/31/89.
160. Singhal, G. H.; Colle, K. S.; Edelson, E. H.; Wilson, B. L.; Dao, L. H. "Hydroconversion of Carbonaceous Material" US Patent 4561964, 12/31/85.
161. Howell, J. A.; Kukes, S. G. "Mixture of a Molybdenum Carboxylate and a Molybdenum Dithiophosphate or a Molybdenum Dithiocarbamate for Use in a Hydrovisbreaking Process" US Patent 4705766, 11/10/87.
162. Howell, J. A.; Kukes, S. G. "Hydrovisbreaking of Oils", US Patent 4708784, 11/24/87.
163. Kukes, S. G.; Howell, J. A. "Hydrofining of Oils" US Patent 4802972, 2/7/89.
164. Howell, J. A.; Kukes, S. G. "Hydrovisbreaking Process for Hydrocarbon Containing Feed Streams" US Patent 4608152, 8/26/86.
165. Lang, R. J.; Maa, P. S.; Lavanga, V. R. "Catalysts Comprising Metal Compounds on Carbon Support" US Patent 4831003, 5/16/89.
166. Chen, H. H.; Montgomery, D. S.; Strausz, O. P. "Hydrocracking of Athabasca Bitumen Using Oil-Soluble Organometallic Catalysts. Part II: Comparison of Metal Naphthenates and Metal Acetylacetonates with Nickel Carboxylate as Oil-Soluble Liquid-Phase Hydrocracking Catalysts" AOSTRA Journal of Research, 1988, 4, 143-152.
167. Ojima, Y.; Sasaki, Y.; Kondo, T.; Ukegawa, K.; Matsumura, A.; Koguchi, K.; Takahashi, T. "Hydrocracking of Heavy Oils with a Highly Dispersed Molybdenum Catalyst" Kogai Shigen Kenkyusho Iho, 1985, 15, 1-8.
168. Ho, T. C. "Effect of Sulfiding on an Unsupported Cobalt-Molybdenum Hydrotreating Catalyst" J. Catalysis, 1991, 131, 298-299.
169. Eltzner, W.; Breysse, M.; Lacroix, M.; Leclercq, C.; Vrinat, M.; Diemann, E. "A New Highly Active Hydrotreating Catalyst Prepared by the Decomposition of Thiotungstonickelate and Characterized by High Resolution Electron Microscopy" Polyhedron, 1988, 7, 2405-2409.
170. Masuyama, T.; Kageyama, Y.; Kawai, S. "A Ca-modified Ni-Mo Catalyst for Hydroprocessing of Coal Liquid Bottoms in Two-Stage Coal Liquefaction" Fuel, 1990, 69, 245-250.
171. Baker, J. R.; McCormick, R. L.; Haynes, H. W. "The Effect of Sodium Impregnation on Ni-Mo/Al₂O₃ Catalyst Performance When

- Hydrotreating a Coal-Derived Liquid" *Ind. Eng. Chem. Res.*, 1987, 26, 1895-1901.
172. Ehlers, J.; Budahn, P. "Catalyst-Containing Coal for Use in Liquid-Phase Hydrogenation" US Patent 4495306, 1/22/85.
 173. Dolkemeyer, W.; Giehr, A.; Keim, K. H.; Lenz, U.; Ritter, G. "Catalyst for Hydrogenation of Slurried Coal" German Patent 3108798, 9/16/82.
 174. Fouda, S. A.; Kelly, J. F. "Hydrocracking of Coal Slurries" Canadian Patent 1276902, 11/27/90.
 175. Bisaria, M. K.; Bakhshi, N. N.; Ranganathan, R. "Recent Advances in Heavy Oil Upgrading Research" AIChE 1990 Spring National Meeting, Orlando, Preprint N. 90b, 44 p.
 176. Rahimi, P. M.; Fouda, S. A.; Kelly, J. F. "Coproprocessing Using H₂S as a Promoter" *Fuel*, 1987, 66, 1215-1218.
 177. Rahimi, P. M.; Fouda, S. A.; Kelly, J. F.; Malhotra, R.; McMillen, D. F. "Characteristics of CANMET Coprocessing Distillates at Different Coal Concentrations" *Fuel*, 1989, 68, 422-429.
 - 177a. Fouda, S. A.; Kelly, J. F.; Rahimi, P. M. "Effects of Coal Concentration on Coprocessing Performance" *Energy & Fuels*, 1989, 3, 154-160.
 178. Itoh, T.; Tsuchida, Y. "New Catalyst for Hydrocracking of Vacuum Residue" *Appl. Catal.*, 1989, 51, 213-222.
 179. Kondo, T.; Sakabe, T.; Konishi, H.; Ojima, Y.; Ukegawa, K.; Matsumura, A. "Hydrocracking of Heavy Oils with Fine Powder Catalysts--6. Hydrocracking of Oil Sand Bitumen with Discharged HDS Catalyst" *J. Jpn. Pet. Inst.*, 1983, 26, 44-49.
 180. Aitchison, D. W.; Clark, P. D.; Fitzpatrick, E.; Hawkins, R. W.; Lee, T. L. K. "The Liquefaction of Alberta Subbituminous Coals with Iron-Sulphur Catalyst Systems" *Fuel*, 1986, 65, 603-607.
 181. Wang, L.; Cui, Z.; Liu, S. "The Application of Moessbauer Spectroscopy to the Study of Coal Liquefaction with Fe Catalyst" *Fuel* 1992, 71, 755-759.
 182. Nippon Kattan Ekika, "Liquefaction of Coal with Reduced Level of Sulfur" Japanese Patent J03131683, 6/5/91.
 183. Garg, D.; Sunder, S. U.S. Patent No. 4,626,342, December 2, 1986, Assigned to Air Products and Chemicals.
 184. Garg, D. "Coal Liquefaction by Hydrogen and Solvent" US Patent 4441983, 4/10/84.

185. Kim, H.; Curtis, C. W. "Reaction Pathways of Model Coprocessing Systems Using Molybdenum Naphthenate and Excess Sulfur" *Energy & Fuels*, 1990, 4, 206-214.
186. Kim, H.; Curtis, C. W. "Interactive Chemistry of Coal-Oil Reactions Using Model Systems" *Energy & Fuels*, 1990, 4, 214-219.
187. Kamia, Y.; Nobusawa, T.; Futamara, S. "Catalytic Effects of Iron Compounds and the Role of Sulfur in Coal Liquefaction and Hydrogenolysis of SRC" *Fuel Proc. Tech.*, 1988, 18, 1-10.
188. Garcia, A. B.; Schobert, H. H. "Effects of Organic Sulfur Content on Thermolysis and Hydrogenolysis of Lignites" *Fuel Proc. Tech.* 1990, 24, 179-185.
189. Cook, P. S.; Chuan, L/ S.; Sheng, H. G.; Jackson, W. R.; Cassidy, P. J. "Mossbauer Study of the Effect of Organic Sulphur on the Catalysis of the Hydroliquefaction of Victorian Brown Coal" *Fuel* 1988, 67, 942-948.
190. Waqif, M.; Bachelier, J.; Saur, O.; Lavalley, J.-C. *J. Mol. Catal.* 1992, 72, 127.
- 190a. Wen, M. Y.; Wender, I.; Tierney, J. W. "Hydroisomerization and Hydrocracking of n-Heptane and n-Hexadecane on Solid Superacids" *Energy & Fuels* 1990, 4, 372-379.
191. Kotanigawa, T.; Takahashi, H.; et. al. "The Mechanism for Formation of Sulphate in Sulphur-Promoted Iron Oxide Catalysts for Coal Liquefaction" *Fuel* 1988, 67, 927-931.
192. Nagase, Y.; Jin, T.; Hattori, H.; Yamaguchi, T.; Tanabe, K. *Bull. Chem. Soc. Jpn.* 1985, 58, 916.
193. Yamaguchi, T.; Jin, T.; Tanabe, K. "Structure of Acid Sites on Sulfur-Promoted Iron Oxide" *J. Phy. Chem.* 1986, 90, 3148-3152.
194. Pradhan, V.; Tierney, J. W.; Wender, I. "Sulfur-promoted Metal Oxides as Coal Liquefaction Catalysts" ACS 200th National Meeting, Washington, DC, ACS Div. Fuel Chem. Preprints, 35 #3:793-800, 1990.
195. Pradhan, V. R.; Tierney, J. W.; Wender, I. "Activity, Characterization, and Sintering Behavior of Sulfate Iron Oxides in Liquefaction of Low-Pyrite Coals" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:254-261, 1992.
196. Pradhan, V. R.; Holder, G. D.; Wender, I.; Tierney, J. W. "Kinetic Modeling of Direct Liquefaction of Wyodak Coal Catalyzed by Sulfated Iron Oxides", letter, *Ind. Eng. Chem. Res.*, 1992, 31, 2051-2056.

197. Pradhan, V. R.; Tierney, J. W.; Wender, I. "Catalysis in Direct Coal Liquefaction by Sulfated Metal Oxides" *Energy & Fuels*, 1991, 5, 497-507.
198. Kotanigawa, T.; Yokoyama, S.; Yamamoto, M.; Maekawa, Y. "Catalytic Activities of Sulphate and Sulphide in Sulphur-Promoted Iron Oxide Catalyst for Coal Liquefaction" *Fuel* 1989, 68, 618-621.
199. Agency of Industrial Science and Technology, "Liquefaction of Coal", Japanese Patent J01087686, 3/31/89.
200. Maa, P. S.; Vernon, L. W.; Winter, W. E.; Singhal, G. H. "Hydroconverting Carbonaceous Materials, Especially Coal" US Patent 4824558, 4/25/89.
201. Lovetro, D. C.; Weller, S. W. "Stannous Chloride and Cobalt Molybdate-Alumina Catalysts in Hydrogenolysis of Solvent Refined Coal" *Ind. Eng. Chem., Prod. Res. Dev.* 1977, vol. 16, no. 4, 297-300.
202. Diaz, G.; Luna, R.; et. al. "X-ray Diffraction Study of a CoMo Sulfide Obtained by the Impregnated Thiosalt Decomposition Method" *Catalysis Letters*, 1990, 5, 377-82.
203. Hirschon, A. S.; Horita, Y. et. al. "Promoted Hydrotreating Catalysts" ACS 204th National Meeting, Washington, DC, ACS Div. *Fuel Chem. Preprints*, 37 #4:1864-1870.
204. Tauster, S. J.; Pecoraro, T. A.; Chianelli, R. R. "Structure and Properties of Molybdenum Sulfide: Correlation of O₂ Chemisorption with Hydrodesulfurization Activity" *J. Catalysis*, 1980, 63, 515-519.
205. Chianelli, R. R. "Fundamental Studies of Transition Metal Sulfide Hydrodesulfurization Catalysts" *Catal. Rev. - Sci. Eng.*, 1984, 26, 361-393.
206. Chianelli, R. R. "Amorphous and Poorly Crystalline Transition Metal Chalcogenides" *Int. Rev. Phys. Chem.*, 1982, 2, 127-165.
207. Liang, K. S.; Chianelli, R. R. "Structure of Poorly Crystalline MoS₂ - A Modeling Study" *J. Non-Crystalline Solids*, 1986, 79, 251-273.
208. Stansberry, P. G.; Lin, R.; Lee, C. W.; Terrer, M. T.; Derbyshire, F. J.; Davis, A. "The Structure and Plastic Properties of Coals Following Low-Temperature Catalytic Hydrogenation" 192nd ACS National Meeting, Anaheim, CA, ACS Div. *Fuel Chem. Preprints*, 31 #4:111-118, 1986.
209. Derbyshire, F.; Stansberry, P. "Comments on the Reactivity of Low-Rank Coals in Liquefaction" *Fuel*, 1987, 12, 1741-1742.

210. Burgess, C. E.; Artok, L.; Schobert, H. H. "Relationships of Coal Structure to Molybdenum Catalyst Action in Liquefaction" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:200-206, 1992.
211. Cugini, A. V.; Utz, B. R.; Lett, R. G.; Krastman, D.; Balsone, V. D. "Dispersed Catalytic Approaches in Coprocessing and Coal Liquefaction" AIChE 1990 Summer National Meeting, San Diego, CA, Preprints, N21e.
212. Agency of Ind Sci Tech, Patent No. J62277152-A, Japan, 87.12.02, "Catalyst for Hydrogenation of Heavy Oil -- Comprises Molybdenum Complex Containing Mo, S, and P"
213. Koo, S. M.; Hoppe, M. L.; Laine, R. M. "Heteropolyanions, Soluble Precatalysts for Quinoline Hydrogenation" 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:290-297, 1992.
214. Poulet, O.; Hubaut, R.; Kasztelan; Grimblot, J. "Experimental Evidences of the Direct Influence of Phosphorus on Activity and Selectivity of a MoS_2 - $\gamma\text{Al}_2\text{O}_3$ Hydrotreating Catalyst", Bull. Soc. Chim Belg. vol. 100, 1991, pp. 857-863.
215. Ramirez, J.; Leclercq, C.; Lopez-Agudo, A. "High-resolution Electron Microscopy Study of Phosphorus-Containing MoS_2 - Al_2O_3 Hydrotreating Catalysts" Applied Catalysis A: General, 1992, 83, 251-261.
216. DeCanio, E. C.; Edwards, J. C.; Scalzo, T. R.; Storm, D. A.; Bruno, J. W. "FT-IR and Solid-State NMR Investigation of Phosphorus Promoted Hydrotreating Catalyst Precursors" Journal of Catalysis, 1991, 132, 498-511.
217. Kushiyama, S.; Aizawa, R.; Kobayashi, S.; Koinuma, Y.; Uemasu, I.; Ohuchi, H. "Effect of Addition of Sulphur and Phosphorus on Heavy Oil Hydrotreatment with Dispersed Molybdenum-Based Catalysts" Applied Catalysis, 1990, 63, 279-292.
218. Kushiyama, S.; Aizawa, R.; Kobayashi, S.; Koinuma, Y.; Uemasu, I.; Ohuchi, H. "A Novel Effect of Phosphorus Addition on the Activity of Dispersed Molybdenum-Based Catalysts in Heavy Oil Hydrotreatment" Ind. Eng. Chem. Res. 1991, 30, 107-111.
219. Lewis, J. M.; Kydd, R. A. "The MoO_3 - Al_2O_3 Interaction: Influence of Phosphorus on MoO_3 Impregnation and Reactivity in Thiophene HDS" J. Catal. 1992, 136, 478-486.
220. Lewis, J. M.; Kydd, R. A.; Boorman, P. M. "An Investigation of P Promotion in Ni-Mo/ Al_2O_3 Catalysts" Stud. Surf. Sci. Catal. 1992, 73, 45-50.

221. Garg, D.; Givens, E. N. "Higher-Yielding Coal Liquefaction Process Uses Catalyst Mixture" US Patent 4411766, 10/25/83.
222. Derbyshire, F.; Hager, T. "Dispersed Catalysts for Coal Dissolution" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:312-319, 1992.
223. Stohl, F. V. "The Effects of Iron Sulphide Surface Area Variations on Coal Liquefaction" Fuel 1983, 62, 122-126.
224. Brooks, D. G.; Guin, J. A.; Curtis, C. W.; Placek, T. D. "Pyrite Catalysis of Coal Liquefaction, Hydrogenation, and Intermolecular Transfer Reactions" Ind. Eng. Chem. Process Des. Dev., 1983, 22, 343-349.
225. Farcasiu, M.; Smith, C.; Pradhan, V. R.; Wender, I. "Iron Compounds and Iron Catalysts: Activity in Reactions Relevant to Direct Coal Liquefaction" Fuel Proc. Tech. 1991, 29, 199-208.
226. Wang, H. P.; Lo, R.; Sommerfeld, D. A.; Huai, H.; Pugmire, R. J.; Shabtai, J.; Eyring, E. M. "Spectroscopic Studies of Coal Maceral Depolymerization Effected by an Iron-Based Catalyst" Fuel, 1992, 71, 723-729.
227. Tarrer, A. R.; Shridharan, K. G. "Coal Hydrogenation with Donor Solvent" US Patent 4374016, 2/15/83.
228. Yamashita, H.; Ohtsuka, Y.; Yoshida, S.; Tomita, A. "Local Structures of Metals Dispersed on Coal. 1. Change of Local Structure of Iron Species on Brown Coal During Heat Treatment" Energy & Fuels, 1989, 3, 686-692.
229. Suzuki, T.; Yamada, H.; Sears, P. L.; Watanabe, Y. "Hydrogenation and Hydrogenolysis of Coal Model Compounds by Using Finely Dispersed Catalysts" Energy & Fuels, 1989, 3, 707-713.
230. Olson, E. S.; Yagelowich, M. L. "Catalytic Reactions of Sulfided Iron- and Mixed Metal-Pillared Clays" ACS 203rd National Meeting, San Francisco, CA, ACS Div. Fuel Chem. Preprints, 37 #1:262-267, 1992.
231. Huffman, G. P.; Ganguly, B.; Taghiei, M.; Huggins, F. E.; Shah, N. "Structure and Dispersion of Iron-Based Direct Coal Liquefaction Catalysts" ACS 210st National Meeting, Atlanta, GA, ACS Div. Fuel Chem. Preprints, 36 #2:561-569, 1991.
232. Srinivasan, R.; Keogh, R. A.; Davis, B. H. "Characterization of Iron and Sulfided Iron Oxide Catalysts by Electron Microdiffraction" ACS Div. Fuel Chem. Preprints, 37 #3:1265-1271, 1992.

233. Klepel, G.; Kunze, P.; Sommer, H.; Bohlmann, D.; Eckart, V.; Hesse, F.; Bauch, J. "Hydroliquefaction of Coal" German Patent 250940, 10/28/87.
234. Garg, D. "Coal Liquefaction by Hydrogenation Using Iron Catalyst" DE Patent 3414788, 10/25/84.
235. Bacaud, R. "Evaluation of Catalytic Activity in Hydroliquefaction" *Fuel Proc. Tech.* 1991, 28, 203-219.
- 236a. Asahi Chemical Industries, "Coal Liquefaction by Hydrogenating Coal Slurry" Japanese Patent 57042790, 3/10/82.
- 236b. Asahi Chemical Industries, "Liquefaction by Hydrogenation of Particulate Coal" Japanese Patent 57042789, 3/10/82.
- 236c. Asahi Chemical Industries, "Coal Liquefaction by Hydrogenating Slurry" Japanese Patent 57042788, 3/10/82.
237. Davis, A.; Schobert, H. H.; Derbyshire, F. J. "Enhanced Coal Liquefaction by Low-Severity Catalytic Reactions" Technical Progress Report, March to May 1988, DOE/PC/90910-6.
238. Cook, P. S.; Cashion, J. D. "Interactions of Iron- and Tin-Based Promoters During Brown Coal Liquefaction" *Fuel*, 1988, 67, 1428-1435.
239. Sommer, H.; Schlutter, E.; Kunze, P.; John, H. "Preparation of Catalyst for Sump Phase Hydrogenation of Coal" German Patent 285725, 1/3/91.
240. Agency of Industrial Science and Technology, "Catalyst for Coal Liquefaction Reaction" Japanese Patent 032442243, 10/29/91.
241. Garg, D. "Catalyst for Hydroliquefaction of Coal in Hydrogen Donor Solvent" US Patent 4617106, 10/14/86.
242. Sommer, H.; Kunze, P.; Hesse, G.; Wallach, D.; Zimmermann, G.; Anders, K.; John, H.; Becker, K. "Treating Heavy Hydrocarbon Feed" German Patent 263534, 1/4/89.
243. Weller, S.; Pelipetz, M. G. "Coal Hydrogenation Catalysts. Studies of Catalyst Distribution" *Ind. Eng. Chem. Eng. Proc. Dev.* 1951, 43, 1243-1246.

END

**DATE
FILMED**

9/2/93