

AD-A105 667

DELAWARE UNIV NEWARK CENTER FOR CATALYTIC SCIENCE AN--ETC F/6 8/7
DEVELOPMENT OF SUPERIOR DENITROGENATION AND ISOMERIZATION CATAL--ETC(U)
AUG 81 J R KATZER, A B STILES, H KWART N00019-80-K-0507

UNCLASSIFIED

NL

1 of 1
AD A
01687

END
DATE
FILMED
11-81
DTIC

12

LEVEL II

AD A105667

DEVELOPMENT OF SUPERIOR DENITROGENATION
AND ISOMERIZATION CATALYSTS FOR PROCESSING
CRUDE OIL DERIVED FROM SHALE. PART I

Final Report on Project N00019-80-K-0507
for Naval Air Systems Command

Interim Report on Total
Project. This Report Covers
Start-up Period of Assembling
Equipment and Personnel

DTIC
ELECTE
OCT 16 1981
B

15 AUG 81

by

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

Principal Investigators:

James R. Katzer

Harold Kwart

Alvin B. Stiles

15 AUGUST 1981

DTIC FILE COPY

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

412 575 94

81-80-100-1000

DEVELOPMENT OF SUPERIOR DENITROGENATION
AND ISOMERIZATION CATALYSTS FOR PROCESSING
CRUDE OIL DERIVED FROM SHALE. PART I

INTRODUCTION

This study was undertaken and continues primarily because of the following well-known facts:

1. The domestic supply of easily processed light petroleum crude oils is insufficient to meet the needs of the United States.
2. Foreign sources of fuel are undependable for both political and logistic reasons.
3. Shale oil is abundant in the United States and offers the best opportunity of augmenting the inadequate domestic petroleum supply.
4. Shale oil is unusually high in nitrogen and sulfur content and these catalyst poisons and atmospheric pollutants cannot be removed by existing processes, which are successfully applied commercially to light petroleum crude.
5. New catalysts and processes must be developed to successfully process crude shale oil.

It is the thrust of the work performed in Part I of this project to initiate the program. This involved the review of literature as shown in the appended literature and

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

patent references, meetings with people who are knowledgeable in both the analytical and process phases of hydrodenitrogenation, obtaining as complete information as possible about the products from various shale oil recovery processes and finally dove-tailing this work with denitrogenation mechanism studies being concluded concomitantly on model compounds by Center personnel on a DOE project.

It should be emphasized at this time that the first six months' effort supported on Part I was basically the initiation of the project but that this work paved the way for the achievements under Part II currently under way. Part II results will be reported in about three months, but it can presently be said that superior catalysts have been devised and the prospects are bright for still further major improvements.

As a consequence of the fact that Part I involved primarily the initiation of the study, this "final report" will be brief but the "final report" due for Part II in a few months is expected to contain a substantial amount of important new information.

Background to the Development of a Superior Hydrodenitrogenation Catalyst

Much work related to the objective of the project has been performed here at the Center under other projects and naturally becomes a valuable background for this project. In

were agreed to and the equipment was purchased on a conditional basis. The principle involved was total combustion of the sample to form NO_x and the subsequent oxidation of the NO_x to NO_2 with ozone. The NO_2 was passed through a flame and a detector measured luminescence induced by the NO_2 .

It was necessary to make adjustments in the ozonator but when the proper oxygen flow had been derived and the ozonator adjusted, analyses have been rapid and have been reproducible; analysis by other means in other laboratories have corroborated the results.

Analyses for sulfur are also made with the same total combustion facilities. The sulfur is oxidized to SO_2 which is quantized in a suitably calibrated chromatograph.

The analyses are now possible on a routine basis and make it possible to have a three-day cycle for making the test and analyzing the products. Catalyst preparation is done separately by another person (graduate student) assigned to the effort.

Obtaining Samples of Crude Shale Oils

Samples of crude shale oil were obtained from Suntech who had the three types: Paraho, Occidental, Technetics with the complete analyses as tabulated below:

	<u>Ramsbottom No.</u>	<u>Avg. Mol. Wt.</u>	<u>%</u>			
			<u>C</u>	<u>H₂</u>	<u>S</u>	<u>N₂</u>
Paraho	2.5	326	84.3	11.29	0.66	2.18
Technetics	---		84.5	11.69	0.48	1.66
Occidental	---		85.95	12.26	0.91	1.16

<u>Cont.</u>	<u>O₂, %</u>	<u>ppm</u>	
		<u>As</u>	<u>Fe</u>
Paraho	1.16	28	70
Technetics	1.75	20	60
Occidental	1.0	--	--

These are currently being investigated for detoxification but data will be reported at the conclusion of Part II. The samples are being maintained in a sealed bottle and opening and exposure to oxygen is minimized.

Hydrodenitrogenation, Hydrodesulfurization and Isomerization Facilities

These stirred autoclaves were made available from related work on a related project sponsored by the Department of Energy. These facilities are being used for both projects and have served very well. A word of caution should be given however, in that as these facilities age, problems relating to tight seals and closures increase. As a consequence, the maintenance costs are increasing but not to the extent necessary to justify new facilities.

The facilities consist of two high-pressure agitated autoclaves built by Autoclave Engineers but designed or specified by Center personnel. The facilities are capable of operating at pressures to 2500 psi and at temperatures to 450°C. It should be noted parenthetically that the majority of our runs are being made at 500-1000 psi and 350°C but some later runs made under more severe conditions and with the more refractory shale oils indicate that these more severe conditions may be required or desired even with the more effective catalysts. Although our objective is to derive catalysts which are responsive under mild conditions, the overall objective will be to attain optimum efficiency cost-wise.

A test is made by charging the shale oil dissolved in hexadecane to the autoclave with the catalyst suspended as a slurry in this solution. Temperature and pressure are increased to the selected operating conditions and are maintained for the duration of the test. Samples are withdrawn periodically for analyses. The draw-off line is flushed so that the sample taken is representative of the slurry in the autoclave. When appropriate, samples can also be taken from the vapor space to analyze for volatiles such as ammonia, hydrogen sulfide, arsine or other components suspected as being present.

The equipment is thoroughly cleaned between runs to prevent contamination and possible poisoning of subsequent

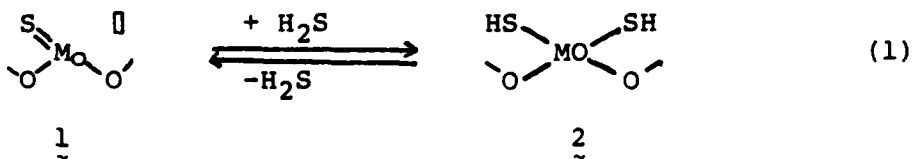
runs. It is noteworthy that there appears to be some severe poison in the crude shale oils which have a very adverse effect on the hydrodenitrogenation reaction. This component "X" is unknown but could be one of many things such as arsenic, alkali, blinding solid or tar. This problem is to be elucidated in Parts II and III of this project.

UTILIZING BACKGROUND INFORMATION DERIVED FROM COMPANION PROJECT ANALYZING DENITROGENATION ROUTES OF SPECIFIC MODEL COMPOUNDS

Background to a Program for Development of a Superior HDN Catalyst

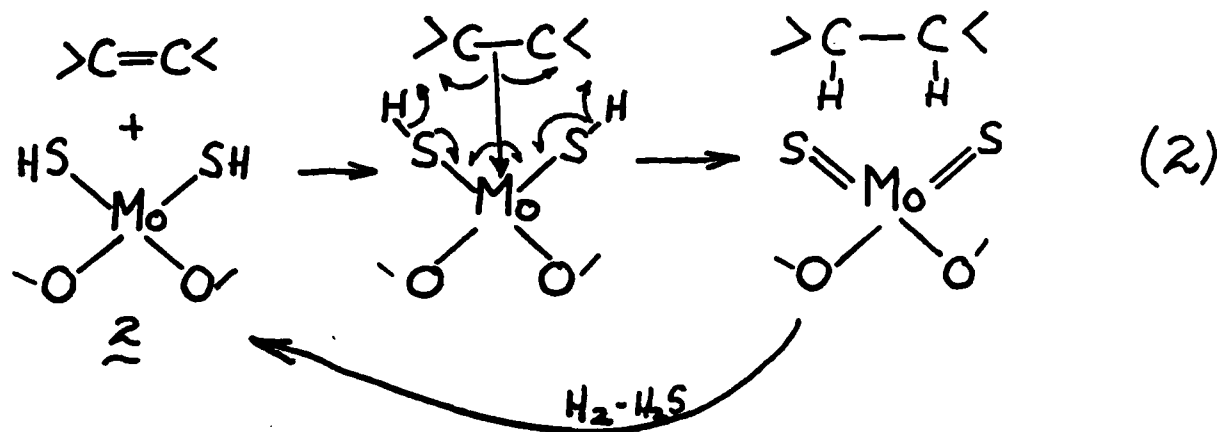
The Structures as the Active Site and the Mechanisms of Action of Sulfided Molybdic Catalysts for HDN

Evidence of both physical (x-ray photoelectron spectroscopy) and chemical nature has accumulated during the past three years showing that there are two fundamental molybdenum-containing structures present in a sulfided molybdcic oxide catalyst and these structures are readily interconverted in high pressures of H₂S. This equilibrium may be expressed by equation (1), where the symbol □ is used to designate an anionic vacancy.



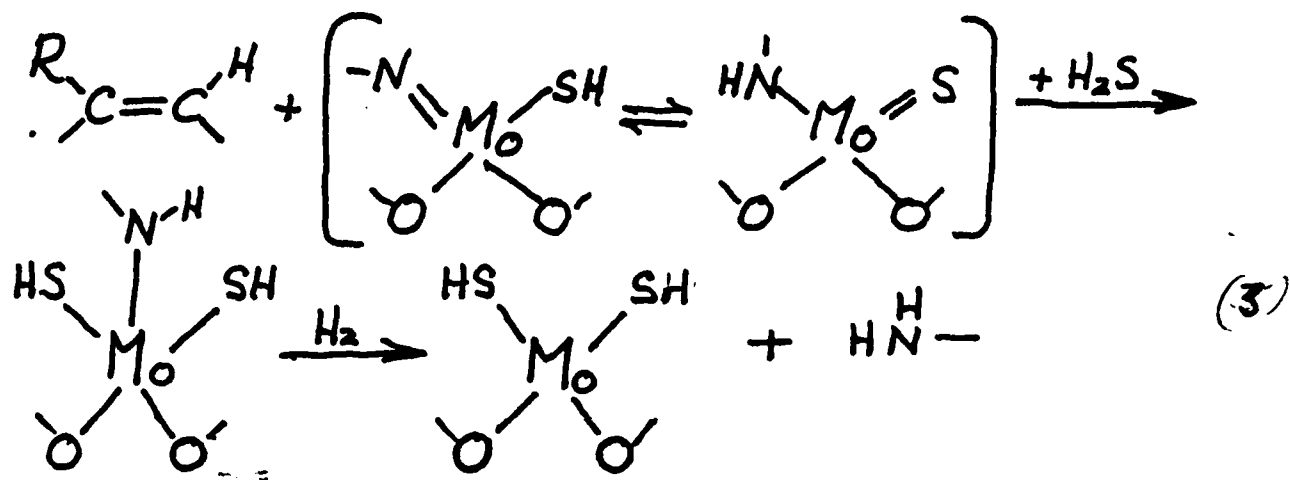
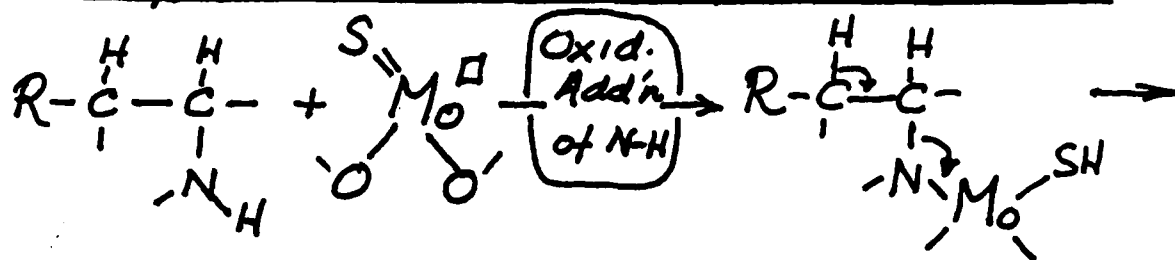
Detailed study of the reaction network for HDN of quinoline has yielded a number of valuable conclusions. One of the most significant among these holds that hydrogenation and hydrogenolysis steps in the network case often occur in quick succession on what appears to be a single active site. Observations of this nature have led to the conclusion that the active site is capable of playing both roles--hydrogenation and hydrogenolysis agent--subject to the activity of other reagents in the medium such as H_2 and H_2S . In this way we have come to recognize that the structure 2 functions in a hydrogenation role, a conclusion for which there is much support in the literature on molybdcic centered catalysts such as the enzyme nitrogenase. The structure 1 has long been implicated as one which is involved with hydrogenolysis activity although there has been some dispute as to how this is effected.

One of the most significant conclusions we have reached in our studies of the quinoline network is that the HDN reaction of an heteroaromatic or aromatic amine requires a preliminary hydrogenation of the aromatic ring. It is only the hydroaromatic, alicyclic or aliphatic amines which can suffer C-N bond breaking in the subsequent hydrogenolysis step. The hydrogenation step appears to occur on the active site via the mechanistic steps depicted in equation (2).

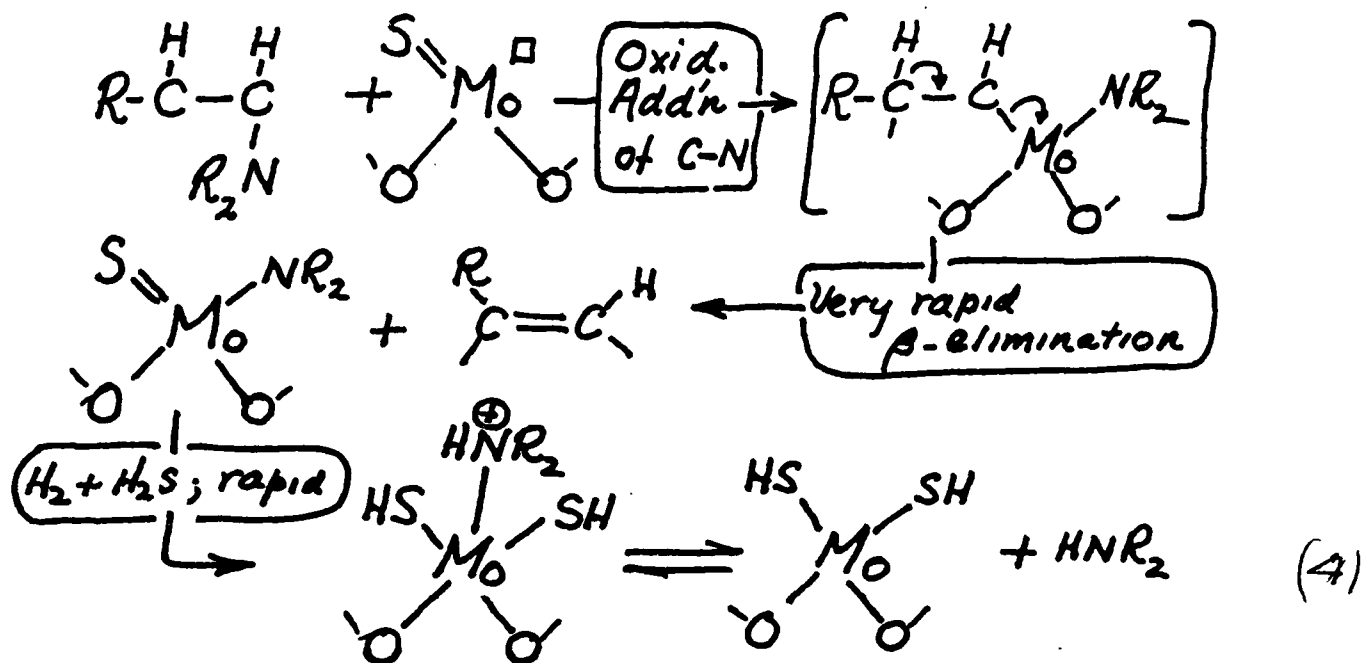


The hydrogenolysis reaction is proposed to be a β -elimination (E-2, Hofmann) brought about by the ability of the catalyst to coordinate the unshared pair on the nitrogen of the amine. There are two courses that could be followed depending on whether we are dealing with a nitrogen-bearing a hydrogen substituent or a tertiary amine nitrogen. In both these possible reactions an oxidative addition (1,1 insertion) of the electron rich molybdenum into the C-N bond occurs. Equation (3) illustrates the mechanistic course of hydrogenolysis with hydroaromatic and aliphatic amines involving oxidative addition to the N-H bond. Equation (4) provides a similar mechanistic scheme for hydrogenolysis via oxidative addition to the C-N bond.

Rapid Reaction of Aliphatic Amines



Direct 1,1 Insertion of C-N Bond



HDN Reactions of Multiring Aromatic
(Heterocyclic) Nitrogen Constituents

It is known that the nitrogenous constituents in shale oil are of the nature of multiring condensed pyridine structures. It behooved us, therefore, to study in what respects, if any, the mechanism of HDN is altered by the addition of aromatic rings to a quinoline nucleus. Moreover, since in quinoline HDN hydrogenation of the aromatic ring appears to be an essential preliminary to breaking the C-N

bond in a subsequent hydrogenolysis reaction, we must ask how the presence of additional aromatic rings affects the rate of overall N-removal; the stoichiometry of hydrogen uptake must also be considered.

Tables I and II provide a listing of the results we have obtained in a short study of the problems presented above, preliminary to undertaking to apply the results to our objective of designing the most efficient HDN process for refining shale oil.

For purposes of immediate application to shale oil, the most important conclusions derived from this preliminary work are the following:

- 1) As with quinoline, total nitrogen removal in multiring condensed heterocycled amines involves hydrogenation of the aromatic rings followed by (an often slower) process of C-N bond scission.

- 2) With multiring substrates of this nature the ring hydrogenation occurs more rapidly than the C-N bond scission reactions leading to the accumulation of considerable concentrations of hydrogenated nitrogen-containing species in the reaction mixture.

- 3) The overall rates of N-removal do not vary significantly because the rates of C-N bond scission in these hydrogenated species are quite similar.

4) The rates of these reactions would appear to be somewhat affected by steric hindrance to adsorption caused by the puckered cyclohexane rings and the similarity of rates must be due to the similarity of the steric effects.

The Significance of our Preliminary Study Results in Determining our Approach to the Catalyst Development Objectives

As summarized above, we have perceived that, aside from an increased stoichiometric requirement for hydrogen (uptake), the size of the multiring heterocyclic components of shale oil do not alter the network character and mechanism of HDN which has previously been elucidated for quinoline. Thus, the reportedly high resistance of shale oils to the HDN process with sulfided, promoted, molybdenic oxide catalysts is not necessarily due to the inherent non-reactivity of its heterocyclic nitrogen constituents. In the light of results obtained in our preliminary study, the rate-determining steps in the HDN of such species must be related to difficulties in hydrogenation and the requirement for taking up a large amount of hydrogen prior to effecting C-N bond breaking. Consequently, the hydrogenation function of the catalyst becomes the most critical one to consider in catalyst design and development.

In this connection also there appears to be still another factor to consider. Since the active site for sulfided

molybdc catalysts (in their hydrogenation function) is one in which the central molybdenum (see structure 2, equation (1)) must coordinate an electron donor species, (in this case the pi electrons of a C=C bond), a hydrogenation poison would be one which could preferentially and tenaciously displace the normal hydrogenation substrate. Shale oil, like all other naturally occurring mixtures, undoubtedly is rich in such potential poisons of the hydrogenation function of the common catalysts used and this could be the reason why shale oil appears to be so refractory to the action of common HDN reaction conditions.

In view of these considerations, we have undertaken the following approaches:




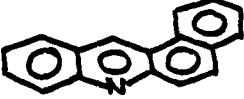

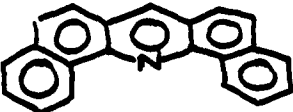
A) If the poisoning components of shale oil should prove to be of organic nature, we would try to subject the shale oil to a preliminary hydrogenation experience. We would attempt to use hydrogenation catalysts that are known to be quite resistant to such poisoning even though they did not possess hydrogenolysis properties. Some candidate hydrogenation catalysts presently being tried are platinum sulfide on charcoal, a well-known catalyst for reducing aromatic amines under relatively mild conditions and known to be resistant to poisoning by sulfur compounds to which most other hydrogenation catalysts (under mild conditions) such as Raney nickel are highly susceptible.

B) If the poisoning components of shale oil should prove to be of largely inorganic nature, such as (for example) arsenic and antimony complexes, we must try to devise a catalyst support or carrier which would be most effective in sequestering the poisonous components and prevent their becoming bound to the active site for hydrogenation. As discussed in the other sections of this report, our efforts in this direction are presently in progress.

CONCLUSION

There are no conclusions to be drawn at this time, but it is expected that when preparing the final report for Part II there will be important conclusions and inferences to present.

TABLE I
STRUCTURE, NOMENCLATURE AND BASICITY OF SELECTED
NITROGEN-CONTAINING COMPOUNDS

<u>Compound</u>	<u>Formula</u>	<u>Structure</u>	<u>pK_a(H₂O) *</u> <u>298 K</u>
Pyridine	C ₅ H ₅ N		5.23
quinoline	C ₉ H ₇ N		4.94
acridine	C ₁₃ H ₉ N		5.60
benz[c]acridine	C ₁₇ H ₁₁ N		4.70
benz[a]acridine	C ₁₇ H ₁₁ N		3.45
dibenz[c,h]acridine	C ₂₁ H ₁₃ N		< 3.45 ^a

^aEstimated from inductive and steric factors influencing (proton) basicity.

TABLE II

REACTIVITY OF SELECTED NITROGEN-CONTAINING COMPOUNDS
TOWARD HDN CATALYZED BY SULFIDED Ni-Mo/ γ -Al₂O₃

<u>Reactant</u>	<u>Time Required for 100% Conversion of Reactant, min</u>	<u>Conversion of Total Organic Nitrogen in 300 min, %</u>	<u>Pseudo First-Order Rate Constant for Total Nitrogen Removal, cm³/g. of Catalyst·hr</u>
pyridine	---	---	~15000
quinoline	145	98	3375
acridine	30	91	2160
benz[c]acridine	45	69	2058
benz[a]acridine	45	67	1451
dibenz[c,h]acridine	5	100	5063

Reaction conditions given in Table I, pseudo first-order rate constant for total nitrogen removal defined by

$$\frac{M_o}{M_c} \frac{dC}{dt} = -KC.$$

Literature References

1. AFAPL-TR-75-10, USAF Tech. Rpt. "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils, Phase 2," Exxon R&E Co., Linden, N.J., May 1976.
2. Aiyar, V. N., O. H. Houwen, and F. W. Bachelor. Distribution of Nitrogen in Fractions of Athabasca Bitumen. *Fuel*, v. 59, April 1980, pp. 276-278.
3. Applied Systems Corp., Vienna, Va. "Compilation of Oil Shale Test Results," ONR Contract N00014-76-C-0427, April 1976.
4. H. Bartick, et al. "The Production and Refining of Crude Shale Oil into Military Fuels," Applied Systems Corp., Vienna, Va., ONR Contract N00014-75-C-0055, August 1975.
5. D. W. Brinkman, M. L. Whisman and J. N. Bowden, Bartlesville Energy Technology Center. Report of Investigation No. 78/23, March 1979.
6. Buell, B. E. Nonaqueous Differential Titration Applied to a Classification of Basic and Very Weak Basic Nitrogen Compounds in Petroleum. *Anal. Chem.*, v. 39, No. 7., June 1967, pp. 756-761.
7. Bungler, J. W., K. P. Thomas, and S. M. Dorrence. Compound Types and Properties of Utah and Athabasca Tar Sand Bitumens. *Fuel*, v. 58, March 1979, pp. 183-195.
8. *Business Week*. Money for Synfuels May Soon Start to Flow. June 1, 1981, pp. 32 and 33.
9. *Business Week*. America's Restructured Economy-Energy. June 1, 1981, pp. 68-74.
10. S. E. Buttrill, Jr. Analysis of Jet Fuels by Mass Spectrometry, in Naval Research Laboratory Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels, Naval Air Systems Command, June 15-16, 1978, and references therein.
11. D. R. Clutter, L. Petrakis, R. L. Stenger and R. K. Jensen. *Anal. Chem.*, 44, 1395 (1972).
12. Cummins, J. J., R. E. Poulson, and W. E. Robinson. Nitrogen Compounds Types in Green River Oil Shale and Its Kerogen Degradation Products. Preprints, ACS Div. Fuel Chem., v. 20, No. 2, 1975, pp. 154-161.

13. H. F. Drushel. Anal. Chem., 49, 932 (1977).
14. Eccles, R. M. and G. R. DeVaux. Current Status of H-Coal Commercialization, Chem. Engr. Progress, May 1981, pp. 80-85.
15. Energy Insider, U.S. Dept. of Energy. Two Experimental Synfuel Plants Complete Extended Continuous Runs. April 27, 1981, pp. 1 and 7.
16. Epperly, W. R., D. T. Wade and K. W. Plumlee. Donor Solvent Liquefaction. Chem. Engr. Progress, May 1981, pp. 73-79.
17. Flinn, R. A., O. A. Larson, and H. Beuther. How Easy is Hydrodenitrogenation? Hydrocarbon Processing and Petrol. Refiner, v. 42, No. 9, September 1963, p. 129 on.
18. Ford, C. D., S. A. Holmes, L. F. Thompson, and D. R. Latham. Separation of Nitrogen Compound Types from Hydrotreated Shale Oil Products on Basic and Neutral Alumina. To be published.
19. (a) J. W. Frankenfeld and W. F. Taylor, Final Report under Naval Air Systems Command Contract No. N-0019-76-0675, Feb. 1979, and references therein; (b) B. Witkop, J. Amer. Chem. Soc., 72, 1428 (1950); (c) B. Witkop and J. B. Patrick, J. Amer. Chem. Soc., 73, 713 (1951); (d) I. Saito, T. Matsuura, M. Nakagawa and T. Hino, Accts. Chem. Res., 10, 346 (1977); (e) R. J. S. Beer, L. McGrath, and A. Robertson, J. Chem. Soc., 3283 (1950).
20. Freel, D. M. Jackson and B. K. Schmid. The SRC-II Demonstration Project. Chem. Eng. Progress, May 1981, pp. 86-91.
21. C. M. Frost and R. E. Poulson. Amer. Chem. Soc., Div. Petroleum Preprints, 20, 176 (1975).
22. Frost, C. M., and H. B. Jensen. Hydrodenitrogenation of Crude Shale Oil. Preprints, ACS Div. Petrol. Chem., v 18, No. 1, 1973, pp. 119-128.
23. Haines, W. E., G. L. Cook, and G. U. Dinneen. Techniques for Separating and Identifying Nitrogen Compounds in Petroleum and Shale Oil. Seventh World Petroleum Cong., Proc., v. 9, 1967, pp. 83-92.
24. (a) R. N. Hazlett, J. M. Hall and M. Matson, Ind.Eng. Chem., Prod. Res. Dev., 16, 171 (1977); (b) D. M. Brown and A. Fish, Proc. Roy. Soc., A308, 547 (1969); (c) N. M. Emanuel, E. T. Denisov and Z. K. Maizus, The Liquid Phase Oxidation of Hydrocarbons, Plenum Press, New York, 1967.

25. Koros, R. M., "Scale-Up Considerations for Mixed-Phase Reactors," to be presented at the NATO multiphase Chemical Reactor Conference, 1981.
26. Koros, R. M., S. Bank, J. E. Hoffman, and M. I. Kay, Hydrodenitrogenation of Shale Oil. Preprints, ACS Div. Petrol. Chem., v. 12, No. 4, 1967, B165-B174.
27. McKay, J. R., J. H. Weber, and D. R. Latham, Characterization of Nitrogen Bases in High-Boiling Petroleum Distillates. Anal. Chem., v. 48, No. 6, May 1976, pp. 891-898.
28. Morandi, J. R., and R. E. Poulson. Nitrogen Types in Light Distillates from Aboveground and In Situ Combustion Produced Shale Oil. Preprints, ACS Div. Fuel Chem., v. 20, No. 2, 1975, pp. 162-174.
29. Poulson, R. E., C. M. Frost, and H. B. Jensen. Characteristics of Synthetic Crude from Crude Shale Oil Produced by In Situ Combustion Retorting. Shale Oil, Tar Sands, and Related Fuel Sources, ed. T. F. Yen, Advances in Chemistry Series, 1976, pp. 1-10.
30. Poulson, R. E. Nitrogen and Sulfur in Raw and Refined Shale Oils. Preprints, ACS Div. Fuel Chem., v. 20, No. 2, 1975, pp. 183-197.
31. T. W. Reynolds. National Aeronautics and Space Administration, Technical Memorandum No. TM-X-3551, June 1977.
32. G. A. St. John, S. E. Buttrill, Jr., and M. Anbar, Ch. 17, "Field Ionization and Field Desorption Mass Spectrometry Applied to Coal Research," in ACS Sym. Series No. 71, Organic Chemistry of Coal, ed. John Larson, 1978.
33. Shah, Y. T., Gas-Liquid-Solid Reactor Design, McGraw-Hill, New York City, 1979.
34. Silver, H. P., N. H. Wang, H. B. Jensen, and R. E. Poulson. A Comparison of Shale-Oil Denitrification Reactions Over Co-Mo and Ni-W Catalysts. Science and Technology of Oil Shale, ed. T. F. Yen, Ann Arbor Science Library Congress, Catalog Card No. 75-10415, ISBN 0-250-400 92-8, 1976.
35. J. Solash, R. N. Hazlett, J. M. Hall and C. J. Nowack. Fuel, 57, 521 (1978).
36. Sonnemans, J, F. Goudriaan, and P. Mars. The Hydrogenolysis of Pyridine on Molybdenum Oxide Containing Catalysts. Paper No. 76 at 5th International Congress on Catalysts, Palm Beach, Fla., 1972.

37. Sullivan, R. F., B. E. Stangeland, D. E. Green, C. E. Rudy, and H. A. Frumkin. Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes. Interim DOE Report, Category UC-90d, No. FE-2315-25, April 1978.
38. Uden, P. C., A. P. Carpenter, Jr., H. M. Hackett, D. E. Henderson, and S. Siggia. Qualitative Analysis of Shale Oil Acids and Bases by Porous Layer Open Tubular Gas Chromatography and Interfaced Vapor Phase Infrared Spectrophotometry. Anal. Chm., v. 51, No. 1 January 1979, pp. 38-43.
39. Vogh, J. W., S. A. Holmes, G. P. Sturm, Jr., P. W. Woodward, and J. E. Dooley. Characterization of Hydro-treated TOSCO Shale Oil. ERDA/BERC RI-77/17, 1977, 18 pp.
40. C. C. Ward, F. C. Schwartz and M. L. Whisman, Technical Report #11 under Ordinance Project TB5-01-010, Bartlesville Energy Technology Center, July 1961.

Promoters for Catalyst

<u>Reference No.</u> <u>(Con't)</u>	<u>Patent</u>	<u>Inventor(s)</u>	<u>Promoter</u>
41	3,345,286 (1967)	J.M. Kovach and S.E. Rogers	Rare earth
42	3,383,305 (1968)	"	Mn as promoter
43	3,383,306 (1968)	"	Vanadium as catalyst
44	3,422,002 (1969)	"	Pt as promoter
45	3,644,197 (1972)	A.E. Kelley and F.C. Wood	Pt as promoter
46	3,723,299 (1973)	H.W. Seitzer	Mn as promoter
47	4,052,296 (1977)	A.A. Montagra	Zinc as promoter
48	4,139,492 (1979)	R.J. Poland and J.D. Voorhies	Fluorobenzoic acid as promoter
49	4,152,251 (1979)	G.A. Michelson	Fluorine as promoter

Catalyst Supports

	<u>Patent</u>	<u>Inventor(s)</u>	<u>Support</u>
50	3,367,862 (1968)	R.B. Mason	Charcoal
51	3,969,273 (1976)	S.M. Brown and D.M. Wallace	Al phosphate
52	4,065,380 (1977)	H.E. Swift and R.F. Vogel	Synthetic mica montmorillonite
53	4,128,505 (1978)	R.J. McKovsky and A.J. Silvestri	TrO ₂ - ZrO ₂

Catalysts

	<u>Patent</u>	<u>Inventor(s)</u>	<u>Novelty</u>
54	3,639,268 (1972)	J. Jaffe and J.R. Kolvell	Fluorine containing alumino silicate
55	3,676,332 (1972)	M.M. Johnson and D.C. Tabler	Molybdenum arsenic as catalyst

DATE
ILME