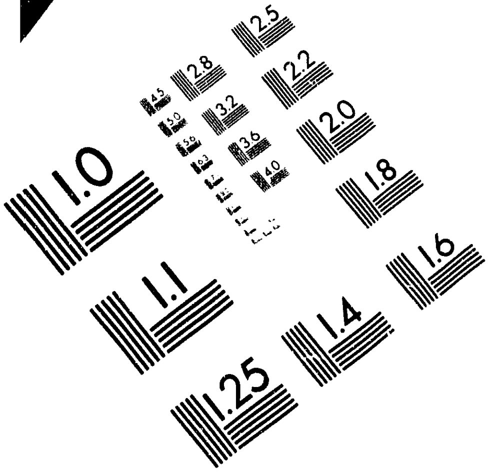

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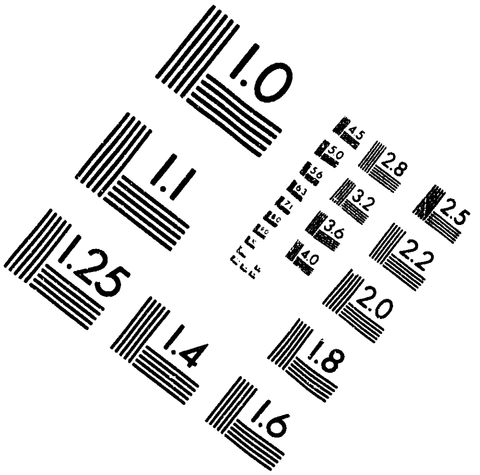

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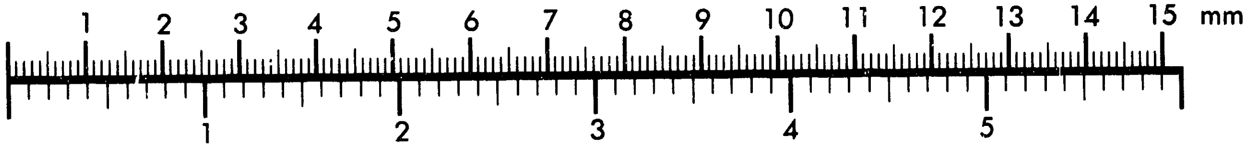

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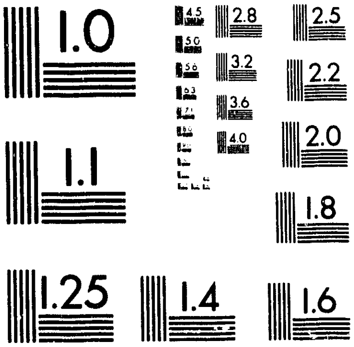

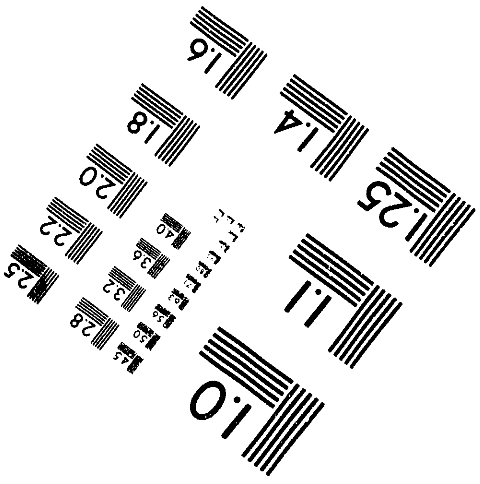

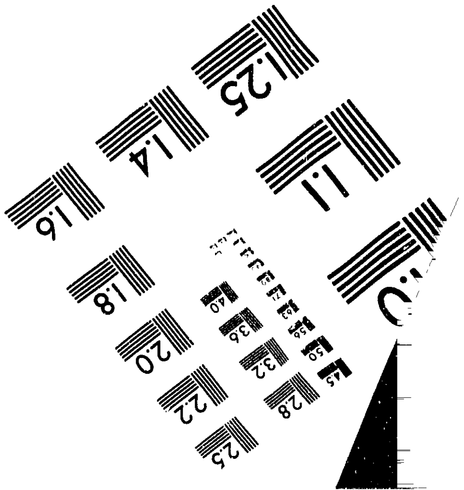

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TRANSITION METAL CATALYSIS IN THE GENERATION OF PETROLEUM AND NATURAL GAS

PROGRESS REPORT

Department of Energy Grant DE-FG05-92ER14295

Frank Mango, Principle Investigator

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PO Box 2692
Houston, TX 77252-2692

PROJECT SUMMARY

Institution:	Rice University
Principal Investigator:	Dr. Frank D. Mango
Title of Project:	Transition metal catalysis in the generation of petroleum and natural gas.

Technical Abstract:

A new hypothesis is introduced for the generation of petroleum and natural gas. The transition metals, activated under the reducing conditions of diagenesis, are proposed as catalysts in the generation of light hydrocarbons. The objective of this proposal is to test that hypothesis. Transition metals (Ni, V, Ti, Co, Fe), in kerogen, porphyrins, and as pure compounds, will be tested under catagenic conditions for catalytic activity in the conversion of normal paraffins and hydrogen into light hydrocarbons. If the hypothesis is correct, kerogenous transition metals should become catalytically active under the reducing conditions of diagenesis and catalyze the conversion of paraffins into the light hydrocarbons seen in petroleum. Moreover, the C_1-C_4 hydrocarbons generated catalytically should be similar in molecular and isotopic compositions to natural gas.

PROGRAM OBJECTIVES

I proposed that the light hydrocarbons in petroleum and natural gas are generated catalytically, rather than thermally, and demonstrating this is the major objective of this research. It was postulated that the transition metals (V, Ni, Co, Fe, Ti, and similar elements) in kerogenous sedimentary rocks, under the reducing conditions of diagenesis, become active Ziegler-Natta (Z-N) catalysts (Mango, 1992), thus converting long-chain paraffins into light hydrocarbons. In theory, Z-N metal catalysis offers a unique kinetic route to methane , and thus a pathway to gas similar in composition to natural gas (Hypothetical Scheme).

The experimental program has three objectives:

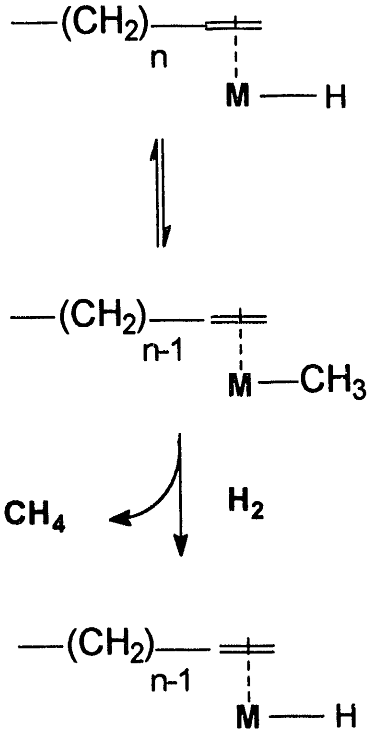
1. Kerogenous transition metals become Z-N active under diagenetic conditions.

2. These metals promote the closure of carbocyclic rings forming the iso- and cycloalkanes seen in petroleum.

3. Metal catalysis provides a facile route to natural gas under the mild conditions of catagenesis (i.e., from 100 to 150° C).

Abstract. Significant progress has been made on two critical objectives. We have shown that kerogenous sedimentary rocks, pretreated with hydrogen, are catalytically active in the generation of light hydrocarbons. The reaction proceeds under mild conditions (< 200^{o}) suggesting that catalysis could be robust on a geologic time scale. Moreover, the catalytic process is remarkably specific in the generation of methane.

HYPOTHETICAL SCHEME



EXPERIMENTAL RESULTS

Construction is now complete on a glass manifold apparatus designed for batch or flow reactions under hydrogen. This system will be used in scale-up reactions to generate products in sufficient amounts for analysis in outside laboratories. The gas chromatography reactor, which functions on mg. samples of catalyst, is now complete and functioning as designed. Both reactors are currently in use analyzing heavy crude oils and kerogenous sedimentary rocks (source rocks) for catalytic activity.

The initial experiments used a heavy California crude oil (Monterey formation) as the transition metal source, dispersed on the walls of a U-tube reactor. The crude was pretreated with flowing hydrogen at 250^{o} C to reduce any metal oxides and to remove volatile components. The system was then reacted with ethylene and hydrogen at various temperatures under 200^{o}C, temperatures at which thermal cracking does not occur, while Z-N catalysis should be vigorous. The strategy here was to have ethylene polymerize on active Z-N sites, thus generating the key intermediates *in situ*. The crude oil was catalytic in the condensation of ethylene, and in the subsequent hydrocracking of the polymer into a variety of light saturated and unsaturated hydrocarbons. Later experiments using octadecene-1 as substrate gave similar products under these conditions supporting the contention that ethylene polymerization precedes catalytic hydrocracking.

Catalysis proceeds with a remarkably high selectivity to methane which was a major product in most cases. In the reaction with octadecene-1 at 180°C, for example, the C_1-C_3 fraction was 30 % methane. This is in sharp contrast to thermal cracking at 600°C where methane concentration is 6% of that fraction (Fabuss *et al., Ind. & Engr. Chem.1,* 293, 1962). The high selectivity to methane persisted in reactions using Monterey source rock (15 % org. C) as catalyst (**Figure**, Ethylene/H_2; 22 hours, 190°C).

CONCLUSIONS AND FUTURE DIRECTIONS

Kerogenous source rocks and heavy crudes display Z-N activity under mild conditions. The active species are surprisingly selective in the formation of methane and other light hydrocarbons in accordance with the hypothetical kinetic scheme described above.

Future experimental work will focus on the activation parameters for methane formation to approximate activity levels between 100 and 150° C, the temperature range for oil and gas generation. These reactions will also be studied for higher olefins, which provide a more direct route to a product similar in overall composition to natural gas.

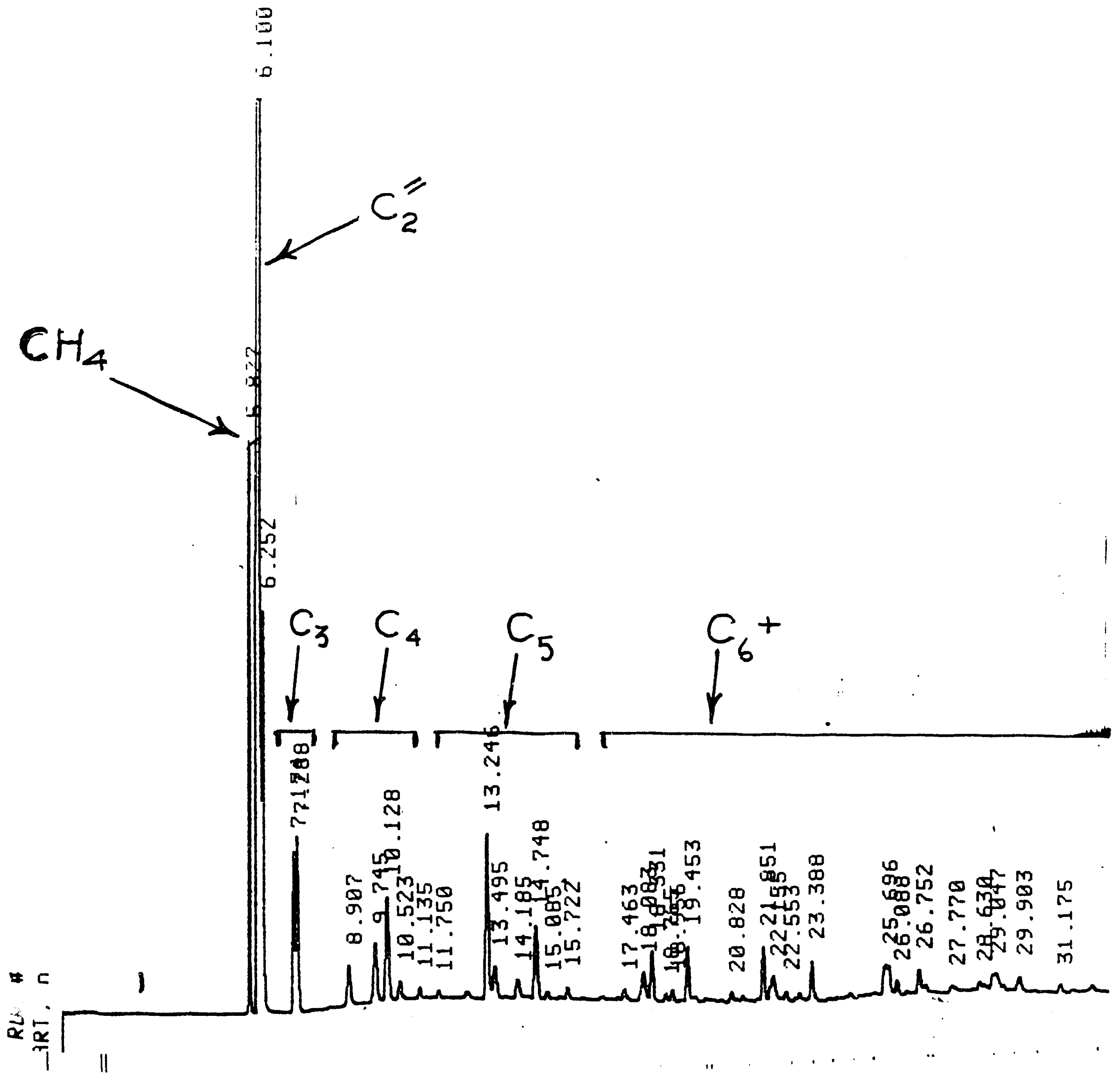


FIGURE Product: $C_2^=$ + H_2 + Source Rock (22 hr., 190°C).

A number of important questions remain unanswered at this time. For example, is hydrogen pretreatment critical and what is the role of water and sulfur? Is oxygen a poison to the catalyst and what is the chemical composition of the species that promotes the surprising selectivity to methane? Finally, the various metals in kerogenous source rocks must be analyzed individually in chemical states (e.g., as sulfides) that approximate their existence in the earth.

It should be stressed that these experimental results constitute our initial exploratory efforts. The practical temperature range for catalysis is yet to be determined and the effects of pressure, physical state (e.g., liquid or polymer) and component concentrations are yet to be established.

PROGRAM STATUS

Experimental work is proceeding in the Chemical Engineering Department of Rice University, rather the Department of Geology & Geophysics, as originally planned. There are two reasons for this change. First, the laboratory facilities in Chem. Engr. are better suited to our experimental needs and, therefore, reduce costs for laboratory renovation. Second, Joe Hightower, Professor of Chemical Engineering, has agreed to collaborate with me in this project. Dr. Hightower brings extensive experience in catalysis to the project, and I am grateful to have him join me in this work.

PUBLICATIONS AND PRESENTATIONS

Two papers have been published in *Geochimical et Cosmochimica Acta (56,* 553-555 & 3851-3854, 1992). Although this work was not completed under DOE sponsorship, it is relevant to the subject of this research and I have included reprints for your information.

I will be giving talks to the Geochemical Division of the American Chemical Society, at the ACS National Spring Meeting, Denver, CO, March 30, 1993 and at the 1993 AAPG Annual Convention in New Orleans, April 27 (Abstracts enclosed). I have also submitted a paper (with J. Hightower) to the European Association of Organic Geochemists for oral presentation at the 16th International EAOG Meeting in Stavanger, Norway, September, 1993 (Abstract enclosed).

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