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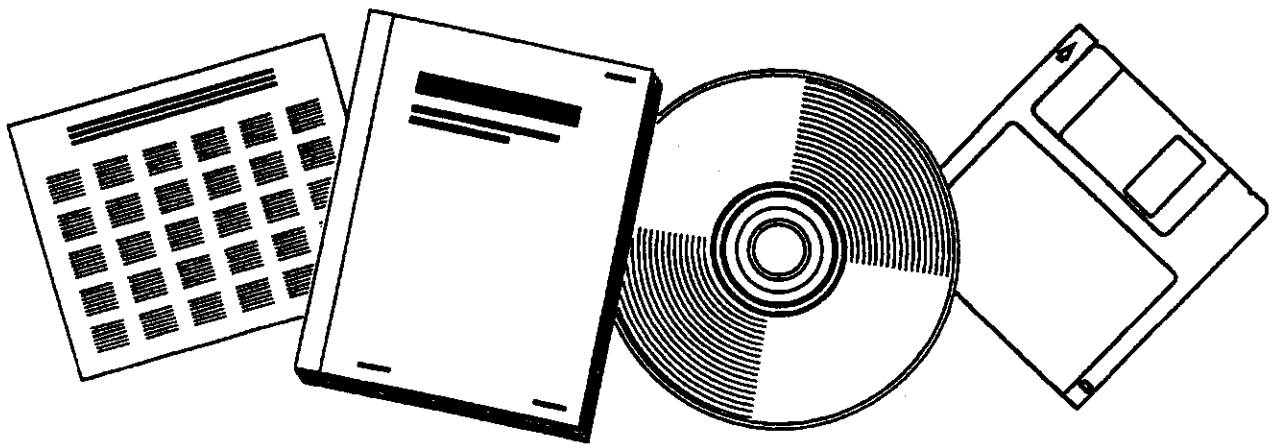
LIQUID HYDROCARBON FUELS FROM SYNGAS. THIRD ANNUAL PROGRESS REPORT, MARCH 1983-FEBRUARY 1984

UNION CARBIDE CORP., TARRYTOWN, NY.
MOLECULAR SIEVE DEPT

1984



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LIQUID HYDROCARBON FUELS FROM SYNGAS

TECHNICAL PROGRESS REPORT
DE-AC22-81PC40077

Third Annual Report
March 1983 - February 1984

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Contents

Appendixes

I. CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals ("Molecular Sieves") in combination with transition metals.

II. SCHEDULE

The contract work was planned for the 36-month period beginning March 6, 1981.

Work on the program is divided into four tasks.

Task 1, essentially completed, was the conversion of low molecular weight liquids, such as methanol and propylene, to gasoline and diesel fuel, with catalysts consisting of only a Molecular-Sieve component, commonly designated as the shape-selective component (SSC).

Task 2 is the conversion of syngas (carbon monoxide and hydrogen) to gasoline and diesel fuel, using catalysts consisting of both a SSC and a transition-metal component (MC).

Task 3 is a study of the surface effects and reaction intermediates present on various catalysts during the hydrogenation of carbon monoxide. This task is conducted under a subcontract with the University of California at Berkeley, and is directed by Dr. Gabor A. Somorjai.

Task 4 comprises the management and technical reports for the contract.

III. ORGANIZATION

Synthesizing "Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysis conducted by the Molecular Sieve Department, Catalysts and Process Systems Division, Union Carbide Corporation.

The work is performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown NY 10591.

Principal investigator is Dr. Jule A. Rabo.

Program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

No work was done on this Task during the March, 1983 through February, 1984 time period covered by this Third Annual Report.

B. Task 2

The work done under Task 2 during the third year showed a steady progression of accomplishments culminated by the catalysts developed during the year's last quarter (December-February, 1984). Consequently, both the run results and evolutionary development of that last quarter's catalysts are discussed in detail.

Eight catalysts were tested from November, 1983 through January, 1984. One catalyst had only water gas shift activity. The other seven catalysts had Fischer-Tropsch synthesis activity from cobalt/thorium intimately mixed with either UCC-101 or UCC-103. This intimate mixture, either alone or promoted with X_4 or X_6, was then used by itself or used with other physically added shape selective and water gas shift components.

The catalysts containing only the intimate mixtures were Co/Th+UCC-101 (Catalyst 1) and Co/Th/X_6+UCC-103 (Catalyst 5). The catalysts containing the intimate mixtures (of the metal component and UCC-103) physically mixed with additional compo-

nents were Co/Th+UCC-103+UCC-101 (Catalyst 2), Co/Th+UCC-103+UCC-108 (Catalysts 3 and 4), Co/Th/X_4+UCC-103+UCC-101 (Catalyst 6), Co/Th+UCC-103+UCC-101+Cu/Zn (Catalysts 8 and 9), and Co/Th+UCC-103+UCC-101+Cu/Zn/Al_2O_3 (Catalyst 10).

The over-riding feature of these catalysts was the high degree of stability achieved from the intimate mixing of the metal component with UCC-103. This behavior, first observed with the Co/Th+UCC-103 catalyst tested during the Eleventh Quarter (Runs 7 and 8), was confirmed by the performance of most of the catalysts tested this quarter. Furthermore, when the additive X_4, found to significantly enhance the poor stability of the physically mixed Co/Th+UCC-101 catalyst (Runs 3 and 9 of the Tenth Quarter), was incorporated into the intimately mixed component of the Co/Th4+UCC-103+UCC-101 catalyst tested this quarter (Catalyst 6), the already good stability found for the Co/Th+UCC-103+UCC-101 catalyst (Catalyst 2 of this quarter) appeared to be improved to the point where there seemed to be negligible deactivation after the initial 100 hours on stream. However, exact quantification of such low deactivation rates will require longer runs that will reduce the presently larger effect of experimental error.

The intimate mixing of the Co/Th with the UCC-101 or UCC-103 gave other characteristics to these catalysts that were not seen in their physically mixed versions. On the positive side, these intimately mixed catalysts produced liquid hydrocarbons that contained less suspended wax and had a lower olefin content. On the negative side, these intimately mixed catalysts had significantly

lower water gas shift activities.

The incorporation of a second shape selective component (either UCC-101 or UCC-108) by its physical mixing with an intimately mixed Co/Th+UCC-103 constituent seemed to change the performance of the intimately mixed constituent only slightly. Such a limited change might be expected from the relative closeness of these two shape selective components to the metal component.

The addition of other ingredients to the intimately mixed Co/Th+UCC-103 constituent was even less satisfactory. The incorporation of additive X_6 failed to reduce the methane yield as it did when it was incorporated into a physically mixed Co/Th+UCC-101 catalyst (Catalyst 4 of the Eleventh Quarterly Report). Furthermore, the addition of water gas shift components not only failed to increase the catalyst's water gas shift activity, but they lowered its Fischer-Tropsch activity as well.

It should be understood that these initial drawbacks for the intimately mixed catalysts are far less important than their achievement of obtaining good stability. Such stability was one of the major goals of this contract. Its accomplishment is a major milestone towards the development of an improved Fischer-Tropsch catalyst.

C. Task 3

The studies at the University of California at Berkeley, under the direction of Professor G. A. Somorjai, have been completed. The final technical report for these studies is presented in Appendix B.

This work covered the hydrogenation of CO on the surfaces of rhodium, rhodium compounds, promoted thorium compounds, rhenium, iron, molybdenum, and potassium-promoted molybdenum, as well as the effect of potassium on small molecular adsorbates on platinum.

V. CHANGES

Modification No. M008 added Albert C. Frost to the list of key personnel. He replaced R. C. Eshenbach as Program Manager.

VI. FUTURE WORK

Efforts during the final quarters will be directed at a continued examination of cobalt catalysts with additional additives to reduce their methane production and increase their water gas shift activity, while maintaining their stability.

Albert C. Frost
Program Manager