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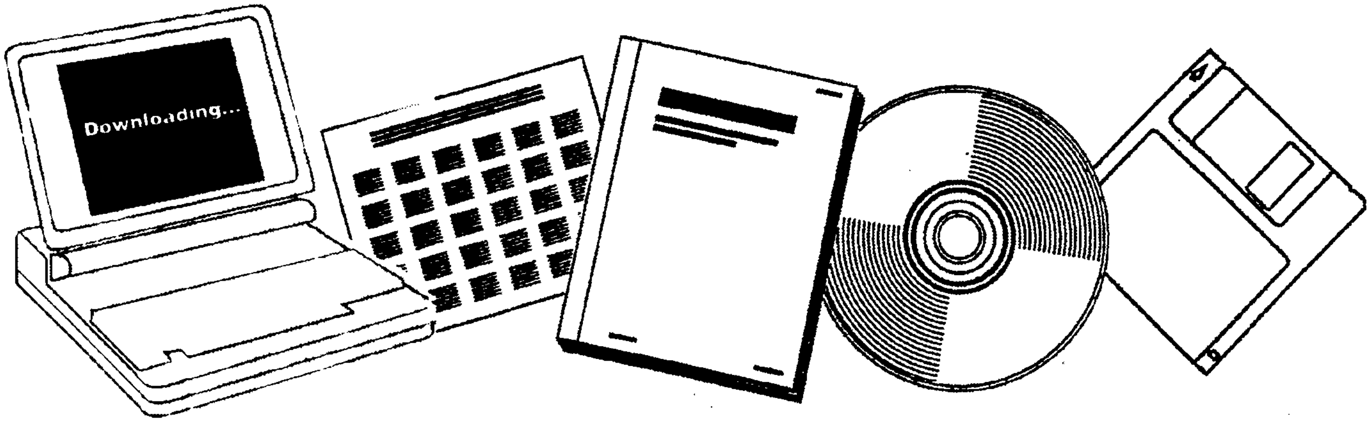
NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION. QUARTERLY TECHNICAL PROGRESS REPORT, 1 JANUARY-31 MARCH 1985

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

DEC 1985



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Air Products and Chemicals, Inc.
Box 538
Allentown, PA 18105
Telephone (215) 481-4911

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25 March 1986

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Technical Information Center
P. O. Box 62
Oak Ridge, TN 37830

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Gentlemen:

Attached are two (2) copies of the approved non-proprietary version of the second quarterly report for DOE contract number DE-AC22-84PC70030, "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production", for the period 1 January 1985 to 31 March 1985.

This quarterly report is suitable for publication.

Sincerely,

W. Eamon Carroll
Program Manager
Technical Diversification R&D

WEC/cr
Attach.

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AIR PRODUCTS

NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

QUARTERLY TECHNICAL PROGRESS REPORT

FOR PERIOD 1 JANUARY - 31 MARCH 1985

W. EAMON CARROLL

NELLIE CILEN

STEPHEN A. MOTIKA

HOWARD P. WITHERS, JR.

AIR PRODUCTS AND CHEMICALS, INC.

ALLENTOWN, PA 18105

MASTER

PREPARED FOR UNITED STATES DEPARTMENT OF ENERGY

UNDER CONTRACT NO. DE-AC22-84PC70030

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EXECUTIVE SUMMARY

In the second quarter of the Air Products and Chemicals, Inc./ United States Department of Energy contract, "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production", work continued on the two major tasks: Task 2 — Development of Improved Supported Catalyst Compositions and Task 3 — Slurry Reactor Kinetic Studies. Work accomplished under Task 2 involved catalyst preparations of cobalt supported on alumina with various levels of promoter. The bimetallic Co/Fe catalyst was again supported on alumina but at higher loadings. Also, in an effort to enhance the water-gas shift reaction, a physical mixture of the standard Co on promoted Al_2O_3 catalyst with a $Cu/Zn/Al_2O_3$ shift catalyst was prepared. Gas phase testing was completed on all of these catalysts. Slurry testing was completed on the basecase Co on promoted Al_2O_3 catalyst as well as on the Ru on promoted Al_2O_3 catalyst, an unpromoted Co on alumina catalyst, and the bimetallic Co/Fe on Al_2O_3 catalyst. Under Task 3, work is in progress to develop a computer program for the analysis of kinetic data from the laboratory reactors.

Task 2 — Development of Improved Supported Catalyst Compositions

Examination of the promoter effect on the Co/Al_2O_3 catalyst was done by preparing and testing catalysts having various Co promoter ratios. As a reference point, an unpromoted catalyst was prepared from $Co_2(CO)_8$ and gammma-Al_2O_3. Two other Co on promoted Al_2O_3 catalysts were prepared having Co/promoter ratios of 1.15 and 0.78. The basecase composition had a Co/promoter ratio of 0.56. Gas phase testing showed that as the Co/promoter ratio increased the bulk activity improved slightly from 27 to 36 moles syngas/kg cat/hr, however, specific activity showed no trend as it varied between 0.24 to 0.31 moles CO/mole Co/min. Hydrocarbon selectivity did show a trend toward lighter products as the amount of promoter was reduced.

As reported last quarter, a Co/Al_2O_3 catalyst was prepared with a different promoter in place of the standard promoter to examine the effect of other promoters on catalyst performance. The gas phase test gave a slightly lower bulk activity of 21 moles syngas/kg cat/hr with a shift in selectivity to ligher products compared to the basecase catalyst.

The Co on promoted Al_2O_3 catalyst had low activity for the water-gas shift reaction and work continued this quarter toward incorporating shift activity into this catalyst. A commercially available, low temperature shift catalyst ($Cu/Zn/Al_2O_3$) was physically mixed with the basecase catalyst and tested in the gas phase reactor. The mixture contained 10 wt% shift catalyst. The gas phase test showed a low bulk activity of 19 moles syngas/kg cat/hr with no indication of enhanced shift activity. There was an increase in oxygenate production, especially of ethanol and higher alcohols. A second gas phase test of the mixed catalysts, this time using pre-activated shift catalyst, had a slight increase in both bulk activity and shift activity. Selectivity moved slightly to higher molecular weight products. However, when a 2-to-1 CO/H_2 feed was used, the shift activity was not good, as reflected by a usage ratio of only 0.35.

Continued study of the bimetallic Co/Fe catalyst involved preparations of somewhat higher metal loadings. The unpromoted catalyst prepared from the Bu_4N^+ salt gave the highest bulk and specific activities of any catalyst tested in the gas phase thus far. The bulk and specific activities were 44 mol syngas/kg cat/hr and 0.49 mol CO/mol metal/min, respectively, at 260°C and CO/H_2 feed of 1.0. Selectivity to straight-run liquid fuel product (C_5-C_{18}) was 64%. Increasing the CO/H_2 feed ratio to 2.0 still resulted in better than basecase activities. The usage ratio was 0.65 and 0.66 for the two different feed ratios. The promoted catalyst, which had a much lower promoter loading than the catalyst tested in the first quarter, was twice as active at 240°C than that heavily promoted catalyst was at 260 to 280°C. It was not as active as the unpromoted catalyst and the resulting hydrocarbon selectivity was similar.

The following four catalysts were screened in the 1 liter stirred autocalves this quarter:

- Co on promoted Al_2O_3
- Ru on promoted Al_2O_3
- Co on unpromoted Al_2O_3
- Co/Fe on unpromoted Al_2O_3

The Co/promoted-Al_2O_3 catalyst slurry test was begun last quarter with the objectives of establishing a baseline for the comparison of other catalysts developed during this contract and determining the extent to which mass transfer resistance is controlling the overall rate of reaction in the 1 liter reactors. No appreciable change in either activity nor hydrocarbon selectivity was attributable to the impeller speed changes from 1200 to 1600 rpm. This indicates that the mass transfer from the gas/liquid interface to the bulk liquid is negligible. Kinetic parameters from the catalysts tested during this contract can therefore be obtained directly from the laboratory data where the impeller speed is 1200 rpm and above.

The Ru/promoted-Al_2O_3 catalyst showed somewhat lower bulk and specific activity than the basecase cobalt catalyst at similar test conditions, except at 280°C where the ruthenium catalyst exhibited a marked increase in specific activity to 0.47 mols CO/mol Ru/min. This was substantially better than 0.22 mols CO/mol Co/min for the basecase cobalt catalyst. Doubling the reactor pressure to 600 psig resulted in a slight increase in activity for the ruthenium catalyst. High yields of liquid fuels, C_5-C_{23} hydrocarbons, in the 66 to 73 wt% range were obtained at 280°C, CO/H_2 of 1.33 to 1.77 and 600 psig. The water-gas shift activity, however, was poor at these conditions. Deactivation of the catalyst at high CO partial pressures may be a problem for this catalyst since the results of the initial screening conditions were not reproduced.

The unpromoted Co on alumina catalyst was tested to determine the role of promoter on activity and hydrocarbon selectivity. The results indicated no apparent effect of the promoter on activity and only a slight positive effect on the liquid product yield. A substantial deactivation was noticeable when the total system pressure was raised to 600 psig from 300 psig. The methane yield increased dramatically from 9.6 wt% at 239°C, 300 psig, $CO/H_2 = 1.50$ and 2.1 L/g/hr to 22.3 wt% at 276°C, 596 psig, $CO/H_2 = 1.0$ and 1.0 L/g/hr with a corresponding decline in activity. High CO partial pressure appears to be detrimental to the performance of this catalyst and will be determined later in other tests of these catalysts.

The alumina supported Fe/Co catalyst behaved much like the unpromoted cobalt catalyst above. The results of this test indicate that low levels of Fe (0.85 wt%) are not adequate enough to enhance either the activity nor hydrocarbon selectivity of this catalyst. The poor water-gas shift activity throughout this study verifies the need for increasing the Fe loading in subsequent catalyst preparations.

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1.0 INTRODUCTION

The future use of coal as a transportation fuel will depend on the development of an economical and energy efficient liquefaction process. The two most advanced processes are the direct liquefaction route involving the dissolution of coal in a solvent aided by a mild hydrogenation and the indirect route in which coal is first gasified to synthesis gas followed by the Fischer-Tropsch reaction. The indirect liquefaction process is the only one currently practiced commercially and, in this respect, has a firm data base of practical experience.

The Fischer-Tropsch reaction, in which carbon monoxide is reduced by hydrogen and polymerized, produces hydrocarbons with a broad range of molecular weights, from methane to paraffin waxes. This creates the need for further downstream processing such as hydrocracking and light olefin oligomerization to maximize the yield of liquid fuel product. Since the discovery of the Fischer-Tropsch reaction, extensive research has been aimed at controlling the product selectivity in order to minimize downstream refining and still remains a prime target for innovation. Previous research has shown that selectivity is mainly controlled by catalyst composition and process conditions. Despite the vast effort in catalyst research, no catalyst has been developed that yields a narrow product distribution of only gasoline or diesel fuel. Because of this, product selectivity has been more successfully controlled by manipulating process conditions.

Since the Fischer-Tropsch reaction is exothermic, control of the reaction heat plays a major role in determining product selectivity. Suspending the catalyst in a liquid medium offers the best means of heat transfer and temperature control. Thus slurry phase operation has been shown to give improved liquid product selectivity mainly by lowering the light gas yield. The amount of data from slurry phase operation, however, is limited to only a few studies and significant differences have been reported in yields, catalyst life and ease of operation. One consistent observation is the lower gas yields and improved gasoline and diesel product selectivity. The improved temperature control has allowed this technology to be useful in converting carbon monoxide-rich synthesis gas from the latest coal gasifiers. Slurry phase operation also appears to be more amenable to scale-up. Much research remains to be done to fully determine the potential of slurry phase Fischer-Tropsch processing and its further development is an important part in our country's program to establish viable technology for converting coal to conventional hydrocarbon fuels.

Under prior contract number DE-AC22-80PC30021 with the Department of Energy, Air Products and Chemicals, Inc. developed several new slurry-phase Fischer-Tropsch catalyst systems that provided enhanced selectivity to liquid fuel products. One group of these catalysts included Co or Ru on a specially promoted/modified support. To further develop and improve these catalyst systems, Air Products, by the current contract to DOE, has begun a program to reproduce, evaluate and characterize these catalysts in detail. Examination of the catalyst kinetics in the slurry phase, along with fuel product characterization will be used to improve process design. Knowledge gained from these studies will provide a basis for the development of novel improved catalysts and process concepts for the selective production of liquid transportation fuels from synthesis gas. Work accomplished in the second quarter is described in this report.

2.0 OBJECTIVE

The major goal of this project is to thoroughly investigate the preparation, characterization and performance of supported and promoted Co and Ru catalysts for use in slurry phase Fischer-Tropsch technology. As this understanding of catalyst behavior increases, improved catalysts will be designed and process concepts developed toward increasing catalyst activity, lifetime and selective production of liquid fuel product. The objectives will be addressed by the following four tasks:

Task 1 — Develop a project work plan which presents the detailed activities to be performed in achieving the objectives of this project. This task has been completed in the first quarter.

Task 2 — Develop improved supported cobalt and ruthenium catalysts by utilizing the promising leads discovered during prior work at Air Products under DOE contract number DE-AC22-80PC30021, which has shown that metals supported on modified aluminas exhibit high activity, stability, and good selectivity to liquid fuels in the slurry phase Fischer-Tropsch process. New catalyst compositions designed to give enhanced selectivity to liquid fuels will also be developed.

In this task, catalysts will be evaluated and tested for their potential to convert synthesis gas into liquid hydrocarbon fuels. Catalysts will be studied by a combination of tests in stirred and fixed-bed reactors and will be evaluated on the basis of activity, selectivity, stability and aging. In addition, catalysts will be characterized by surface and bulk analyses.

Improvements in these catalysts will focus predominantly upon:

- Increasing catalyst activity
- Improving product selectivity for liquid fuels and reducing the yield of methane

- Developing catalyst systems active at high $CO:H_2$ ratios
- Incorporating water-gas shift activity, either directly in the catalyst or utilizing a mixture of catalysts in the slurry

Task 3 — The baseline catalyst compositions derived from both cobalt and ruthenium precursors will be used to establish baseline slurry Fischer-Tropsch rate constants and activation energies. Then the more active and selective slurry catalyst compositions, identified under Task 2, will also be used in deriving slurry FT kinetic parameters. An existing backmixed CSTR model will be used in fitting the kinetic parameters. The kinetic parameters obtained will then be input to a three-phase bubble column computer model in order to predict conversions and space time yields in commercial scale bubble column units under a range of operating conditions.

An attempt will be made to determine kinetic expressions that describe the rate of formation of individual products or product fractions. This will be used to predict space time yields of individual product components or fuel fractions in a commercial scale bubble column.

Finally, mechanistic concepts will be examined, such as olefin reincorporation into growing chains, by adding small amounts of olefins to the feed and determining the effect on product selectivities.

Task 4 — In this task, hydrocarbon product fractions, accumulated from some of the longer slurry tests of the improved catalysts, will be collected under constant process conditions and subjected to a series of tests to evaluate their properties as specification fuel.

3.0 RESULTS AND DISCUSSION

This section contains potentially patentable material and has, therefore, been issued in a supplementary report marked "not for publication".

4.0 EXPERIMENTAL

This section contains potentially patentable material and has, therefore, been issued in a supplementary report marked "not for publication".

5.0 ACKNOWLEDGEMENTS

The skilled technical assistance of P. A. Dotta, G. W. Long, M. Louie and L. E. Schaffer is gratefully acknowledged.

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