



DE88004678

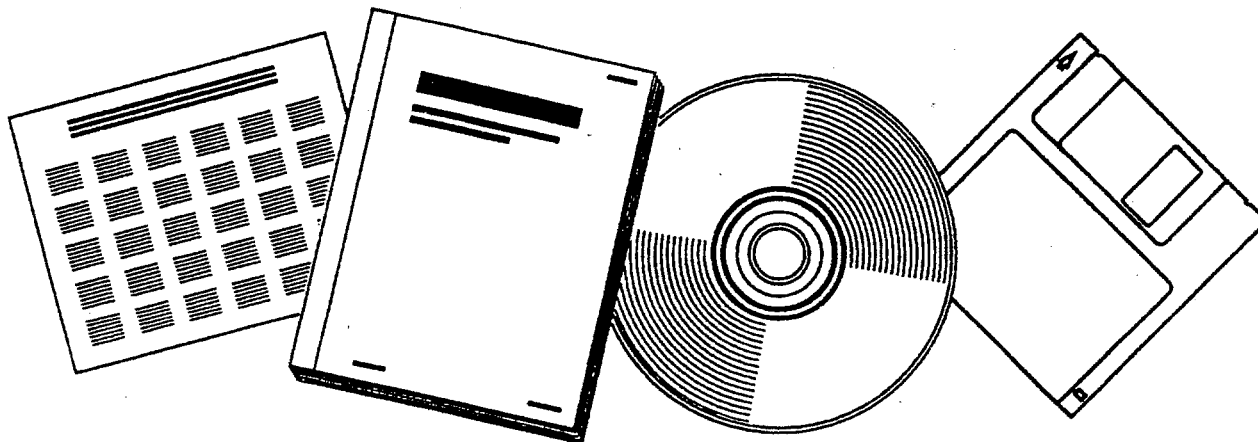
COPY

NTIS[®]
Information is our business.

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

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

DEC 1987



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

DE88 004678

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

FINAL REPORT

REPORT PREPARED BY: H. P. WITHERS, JR.
K. F. ELIEZER
J. W. MITCHELL

CONTRIBUTORS: W. E. CARROLL
D. A. BOHLING
N. CILEN
S. A. MOTIKA

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA 18195

DATE PUBLISHED - DECEMBER 1987

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
UNDER CONTRACT NO. DE-AC22-84PC70030

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express 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 not 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 authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

EXECUTIVE SUMMARY

The preparation, characterization and performance of cobalt and ruthenium carbonyl cluster-based catalysts for use in slurry-phase Fischer Tropsch (FT) technology was investigated. The use of metal carbonyls as active metal precursors allows for the possible control of metal particle size on the support surface and thus offers the potential for better control of activity and selectivity of the FT reaction. Key accomplishments included reproducible catalyst preparation, improvements in activity by use of a silica support, understanding differences between nitrate and carbonyl precursors, and good activity maintenance in the slurry reactor.

A $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ catalyst (3.5% Co, 6.6% Zr) was developed as the most active system in the slurry reactor and also gave the best liquid fuel selectivity. Selectivity patterns correlated to the Schulz-Flory prediction. Silica support provided the highest catalyst activities because it showed the lowest metal-support interaction. For this best catalyst in the slurry reactor, syngas conversion was 25 to 71%, with bulk activity ranging from 16 to 54 mols syngas/kg cat/hr. Selectivity to gasoline range ($\text{C}_5\text{-C}_{11}$) products was 20 to 45% and to diesel range ($\text{C}_{12}\text{-C}_{18}$) products was 17 to 32% in the slurry reactor. These results were obtained under the following conditions: 240°-280°C, CO/H_2 feed = 0.5 - 2.0, 300 psig and space velocity = 1.0-2.0 l/g cat/hr.

This catalyst was successfully tested in an extended slurry-phase run that achieved 6 months on stream with a 10% loss in activity. A kinetic rate expression that took water inhibition into account was derived from the data

of this extended test. An activation energy of 97 kJ/mole was obtained for syngas conversion ranging from 34 to 71% at 240 to 280°C. Diesel fuel product produced by this catalyst was high quality, meeting 9 of 11 ASTM specifications for No. 1-D diesel fuel oil.

The activity of the $\text{Co}_2(\text{CO})_8$ -based catalysts decreased with changing supports as follows: $\text{SiO}_2 \gg \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO} \cdot \text{SiO}_2$. The Co/TiO_2 catalyst gave unusually high selectivity to C_3 - C_4 olefins. Zirconium was found to be the best promoter, compared to Ti, for enhancing activity and selectivity, with the optimum Co/Zr ratio between 0.5 and 1.0. Catalyst activity remained unchanged and eventually declined as the Co loading was increased from 4 to 14%. The Ru catalysts showed the highest activity in the fixed-bed reactor but deactivated rapidly in the slurry reactor. The water-gas shift (WGS) activity of the Co catalysts was not improved by the addition of Cu/Zn WGS catalyst nor by the incorporation of Fe, making these catalysts less attractive for processing CO-rich syngas directly.

The cobalt catalysts have been optimized to some extent during this study but more work must be done, especially with the catalysts having high Co loadings where the potential for very high bulk activity exists. Comparative gas phase tests at constant weight hourly space velocity would be more revealing. Further optimization would require more detailed catalyst characterization, especially the use of a reaction chamber on the ESCA instrument. A method for increasing dispersion at higher metal loadings would be desirable.

Analysis of the data obtained from laboratory Fischer-Tropsch reactors yielded kinetic constants for the following functionality:

$$-r_{CO + H_2} = \frac{k C_{H_2}}{1 + K C_{H_2O} / (C_{CO} C_{H_2})}$$

While other kinetic models resulted in adequate representations of the data, the above model was chosen as best for a variety of physical reasons. The most significant reasons are that this model represents the data quite well over the entire range of collected data and has been shown by other investigators to effectively describe data with high water concentrations (such as is the case here due to the low WGS activity of the catalyst).

While there is a physical basis for selection of this model, it is not possible, with the current data, to statistically discriminate among the rival models. A Bartlett's F-test revealed that it would require sixty data points (with data at the same degree of error as those already reported) to justifiably perform such a discrimination. With tighter error control, through refined analytical measurements, this number of experiments could be reduced significantly.

In the analysis of the kinetic data, catalyst deactivation was assumed to proceed linearly between baseline experiments at fixed temperature. This linear decay assumption proved to be approximately true and allowed elucidation of the intrinsic rate phenomena. The underlying causes of the deactivation are not fully understood. Additional studies are required to determine if the decay is caused by thermal or process effects and the extent to which the decay is reversible. Such studies would ultimately result in the definition of regeneration procedures.

The current study has, therefore, resulted in identification of the most likely kinetic functionality and evaluation of the associated kinetic constants. If the model were to be used for scaleup purposes, additional experiments would be required to ensure that the kinetic parameters were sufficiently accurate. Experimental design techniques could be used in order to minimize the number of runs and to maximize the informative power of the data.

TABLE OF CONTENTS

	<u>PAGE</u>
1.0 <u>INTRODUCTION</u>	1
2.0 <u>OBJECTIVES</u>	3
2.1 Development of Improved Supported Catalyst Compositions	3
2.2 Slurry Reactor Kinetic Studies	6
2.3 Fuel Product Characterization	7
3.0 <u>RESULTS AND DISCUSSION</u>	8
3.1 Development of Improved Supported Catalyst Compositions	8
3.1.1 Basecase Catalyst Preparation and Reproducibility	8
3.1.2 Basecase Catalyst Performance	9
3.1.3 Conventional Catalyst Preparation and Performance	12
3.1.4 Catalyst Activation Studies	13
3.1.5 Promoter Studies	15
3.1.6 Support Studies	17
3.1.7 Metal to Promoter Ratio	18
3.1.8 Metal Loading	19
3.1.9 Other Metals	21
3.1.10 Promotion of Water - Gas Shift Activity	24
3.1.11 Extended Slurry Test	26
3.1.12 Catalyst Characterization	30
3.2 Slurry Reactor Kinetic Studies	32
3.2.1 Olefin Incorporation	32
3.2.2 Kinetic Studies During Slurry Screening Tests	33
3.2.2 Extended Slurry Test Kinetic Studies	36
3.3 Fuel Product Characterization	38

TABLE OF CONTENTS (continued)

4.0	<u>CONCLUSIONS AND RECOMMENDATIONS</u>	40
4.1	Catalyst Studies	40
4.2	Kinetics	41
5.0	<u>EXPERIMENTAL</u>	44
5.1	Catalyst Preparation	44
5.2	Gas-Phase Testing	44
5.3	Slurry-Phase Testing	48
5.4	Product Analysis	50
5.5	Catalyst Characterization	52
6.0	<u>REFERENCES</u>	53
7.0	<u>ACKNOWLEDGEMENTS</u>	55

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	Gas Phase Tests	56
2	Comparative Catalyst Test Data - Slurry Phase	63
3	Basecase Slurry Test Summary - $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$	67
4	Effect of Stirrer Speed	68
5	Effect of Co Source On Activity and Selectivity	69
6	Effect of Syngas Vs. Hydrogen Activation On Hydrocarbon Selectivity	70
7	Zirconium Vs. Titanium as Support Modifier	71
8	Effect of Promoter On Hydrocarbon Selectivity	72
9	Enhanced Olefin Selectivity Using Ti Promoter	73
10	Zirconium Vs. Titanium as Promoter - Slurry Phase	74
11	Support Properties	75
12	Ru Catalyst Performance	76
13	Addition of Cu/Zn/Al Water - Gas Shift Catalyst to Co/Zr/ Al_2O_3 F-T Catalyst	77
14	Addition of $\text{Fe}_3(\text{CO})_{12}$ to $\text{Co}_2(\text{CO})_8/\text{Zr}/\text{SiO}_2$ - Fixed-Bed	78
15	Catalyst Properties	79
16	Selected Kinetic Functionalities	80
17	Summary of Fitted Kinetic Parameters	81
18	Analysis of Slurry-Phase Fischer-Tropsch Synthetic Diesel Fuel	82
19	Detailed Requirements for Diesel Fuel Oils	83
20	ASTM Copper Strip Classifications	83

LIST OF FIGURES (cont'd)

<u>FIGURE</u>		<u>PAGE</u>
24	Hydrocarbon Selectivity - Extended Slurry Test 8862-1-31	107
25	X-Ray Photoelectron Spectra	108
26	X-Ray Photoelectron Spectrum of Fresh $\text{Co}_2(\text{CO})_8/\text{Zr}/\text{SiO}_2$	109
27	Kinetic Data Analysis Program	111
28	Fitting $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ Data	112
29	Activation Energy: $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$	113
30	Linear Fit for Kinetic Model 4	114
31	Parity Plot for Kinetic Model 4	115
32	Catalyst Deactivation: Extended Slurry Test	116
33	Arrhenius Plot: Extended Slurry Test	117
34	Gas Phase Screening System	118
35	Reactor Temperature Measurement	119
36	Continuous, Automated Fischer-Tropsch Slurry Reactor	120
37	Product Analytical Scheme	121

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	Run # 7595-60-C48.4 - Bulk Activity Vs. Time on Stream	84
2	Run # 7595-60-C48.4 - Hydrocarbon Selectivity	85
3	Hydrocarbon Weight Distribution - Sample 7595-60-C48.4-4	86
4	Hydrocarbon Weight Distribution - Sample 7595-60-C48.4-38	87
5	Hydrocarbon Weight Distribution - Sample 7595-60-C48.4-66	88
6	Hydrocarbon Product Distribution	89
7	Effect of Syngas Vs. Hydrogen Activation on Conversion	90
8	Effect of Support on Activity of $\text{Co}_2(\text{CO})_8$ - Based Catalysts (Fixed-Bed Reactor)	91
9	Effect of Surface Area	92
10	Effect of Co/Zr Ratio on Bulk Activity	93
11	Effect of Co/Zr Ratio on Specific Activity	94
12	Effect of Co/Zr Weight Ratio on Slurry-Phase Activity of Co/Zr/Silica Catalysts	95
13	Effect of Cobalt Loading on Bulk Activity of Co/Zr/SiO ₂ Catalyst	96
14	Effect of Co Loading on Co/Zr/SiO ₂ Performance - Slurry Reactor	97
15	Water - Gas Shift Activity	98
16	Bulk Activity Maintenance - Extended Slurry Test 8862-1-31	99
17	Conversion Maintenance - Extended Slurry Test 8862-1-31	100
18	Hydrocarbon Selectivity - Extended Slurry Test 8862-1-31	101
19	Bulk Activity Maintenance - Extended Slurry Test 8862-1-31	102
20	Conversion Maintenance - Extended Slurry Test 8862-1-31	103
21	Hydrocarbon Selectivity - Extended Slurry Test 8862-1-31	104
22	Bulk Activity Maintenance - Extended Slurry Test 8862-1-31	105
23	Conversion Maintenance - Extended Slurry Test 8862-1-31	106