

# ORIGINAL

## DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISHER-TROPSCH CATALYST

### FINAL REPORT

prepared for  
**The U. S. Department of Energy  
Pittsburgh Energy Technology Center**

under  
**Contract No. DE-AC22-91PC91057**

prepared by  
**Robert R. Frame and Hemant B. Gala**

**UOP  
Des Plaines, Illinois**

**February 1995**

# MASTER

Patent cleared by Chicago  
OPC on May 26, 1994.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

35

DE 95009355

### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, 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, trademark, 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.

## TABLE OF CONTENTS

	Page No.
Abstract .....	i
Acknowledgement .....	iii
1. Objectives .....	1
2. Introduction .....	3
2.1 Fischer-Tropsch Background .....	3
2.2 Comparison of Iron and Cobalt Fischer-Tropsch Catalysts .....	5
2.3 Calculations .....	6
2.4 Reaction Mechanism .....	6
2.5 Carbon Number Selectivity .....	10
2.6 Other Fischer-Tropsch Selectivities .....	13
2.7 Cobalt Catalyst Description .....	13
2.8 Reactors .....	16
3. Experimental Summary .....	22
3.1 Introduction .....	22
3.2 Reverse Micelle Catalysts .....	23
3.3 Y-Zeolite Supported Catalysts .....	23
4. Development of Reverse Micelle Catalysts .....	25
4.1 Background .....	25
4.2 Catalyst Preparations .....	26
4.3 Catalyst Supports .....	27
4.4 Catalyst Performance .....	27
4.4.1 Reference Catalyst Performance .....	27
4.4.2 Performance of Catalysts Supported on Magnesium Oxide .....	28
4.4.3 Performance of Catalysts Supported on Carbon .....	30
4.4.4 Performance of Catalysts Supported on Alumina-Titania .....	31

4.5	Stem Analysis .....	31
4.6	Summary .....	33
5.	Development of High Activity Y-Zeolite Supported Catalyst .....	34
5.1	Background .....	34
5.2	Preparation and Evaluation of Catalysts .....	36
5.2.1	Aqueous Impregnations, Steamed but not Acid-washed Y-Zeolite Support .....	36
5.2.2	Aqueous and Reverse Micelle Impregnated Catalysts, Steamed and Acid-washed Y-Zeolite Support .....	37
5.2.3	Ethylene Glycol Impregnations, Steamed and Acid-washed Y-Zeolite Support .....	39
5.2.4	Bound Catalyst: Fixed-bed and Slurry Autoclave Evaluations .....	41
5.2.5	Effect of Changing the Catalyst Reduction Temperature .....	44
5.2.6	Stem Analysis: High Cobalt Catalyst Precursor .....	46
5.2.7	Very High Cobalt Catalysts .....	47
5.2.8	Additional Very High Cobalt Catalysts .....	48
5.2.9	Stem Analysis of a Reduced Very High Cobalt Catalyst .....	52
6.	Conclusions .....	53
7.	Future Directions .....	55
	References .....	57
	Appendix .....	220

## **ABSTRACT**

The reverse micelle catalyst preparation method has been used to prepare catalysts on four supports: magnesium oxide, carbon, alumina-titania and steamed Y zeolite. These catalysts were not as active as a reference catalyst prepared during previous contracts to Union Carbide Corp. This catalyst was supported on steamed Y zeolite support and was impregnated by a pore-filling method using a nonaqueous solvent.

Additional catalysts were prepared via pore-filling impregnation of steamed Y zeolites. These catalysts had levels of cobalt two to three and a half times as high as the original Union Carbide catalyst. On a catalyst volume basis they were much more active than the previous catalyst; on an atom by atom basis the cobalt was about of the same activity, i. e., the high cobalt catalysts' cobalt atoms were not extensively covered over and deactivated by other cobalt atoms.

The new, high activity, Y zeolite catalysts were not as stable as the earlier Union Carbide catalyst. However, stability enhancement of these catalysts should be possible, for instance, through adjustment of the quantity and/or type of trace metals present.

STEM (Scanning Transmission Electronic Microscopy) analysis was a very useful tool during this work. It allowed determination of the size and atomic composition of cobalt crystallites. During the work with high cobalt Y zeolite catalysts STEM analysis showed that some (large) crystallites were present outside of the zeolite matrix in addition to the expected smaller ones present within

the zeolite pores. Furthermore, STEM analysis showed that the trace component zirconium was not evenly distributed across the variously-sized cobalt crystallites. Specifically, it was more likely to be found within the small crystallites in the zeolite pores than in the large ones extraneous to the pores. Since zirconium is added to stabilize the catalyst, solving the stability problem above might, therefore, be as simple as achieving a better zirconium distribution throughout the crystallites.

A primary objective of this work was determination whether small amounts of ruthenium could enhance the activity of the cobalt F-T catalyst. The reverse micelle catalysts were not activated by ruthenium, indeed STEM analysis provided some evidence that ruthenium was not present in the cobalt crystallites. Ruthenium did not seem to activate the high cobalt Y zeolite catalyst either, but additional experiments with Y zeolite-supported catalysts are required. Specifically, cobalt and cobalt/ruthenium catalysts should be re-made in stable versions to allow good assessment of initial catalyst activity. Such catalysts should be evaluated at high space velocities so that only moderate initial conversions result. Under the standard screening test used in this work initial conversions with the high cobalt catalysts were very high with or without ruthenium. The initial deactivation rates also appeared to be high. Thus accurate initial activities could not be determined. It is possible that cobalt-ruthenium catalysts were most active but appeared less active than cobalt-only catalysts during a run because they exhibited a faster deactivation rate.

Should ruthenium prove not to be an effective promoter under the simple catalyst activation procedure used in this work, more complex activation procedures have been reported which are claimed to enhance the cobalt/ruthenium interaction and result in activity promotion by ruthenium.

## **ACKNOWLEDGEMENT**

The authors express their gratitude to Dr. Jule Rabo and Prof. Dr. Hans Schulz for helpful discussions. Furthermore, Prof. Schulz generously furnished us with a copy of the three volume Schering report on the Fischer-Tropsch process.

Dr. Hayim Abrevaya was the principal investigator during the early stages of this contract and was available as a consultant throughout.

Tony Polak, then of UOP, wrote an in-house review of Fischer-Tropsch related surface science studies in 1982. This has been useful throughout this contract and particularly so as background in writing the final report.

In addition to the undersigned, the Fischer-Tropsch team at UOP included at various times the following individuals: Dr. Hayim Abrevaya, Dr. Michael Quick, Dr. Alan van Til, Dr. Susan Lambert, Dr. Steven Bradley, Dr. Michelle Cohn, Frank Dobbs, William Targos, Elaine Schumacher, Sheila Adami, Robert Wasberg, Mark Heynis, Steve Bass and Kevin Kocis.

Finally, we acknowledge the team at DOE, both from the PETC and Washington, D.C. offices for their helpful support during this work.

Robert R. Frame      Hemant B. Gala