FINAL

DOE/PC/93066--T3

# QUARTERLY TECHNICAL PROGRESS REPORT
(July-September, 1994)

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| **CONTRACT TITLE:** | MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES |
| **Contract Number:** | DE-AC22-93PC93066 |
| | University of Kentucky, Lexington, KY |
| **Contract Date:** | Jan 12, 1994 |
| **Anticipated Completion Date:** | Jan 11, 1997 |
| **Government Award:** | $ 64679.00 (for 1994) |
| **Program Manager:** | Dr. Gary J. Stiegel<br>U.S. DOE, PETC, Pittsburgh |
| **Principal Investigators:** | Prof. Gerald P. Huffman, (PI)<br>Dr. K.R.P.M.Rao, (Co-PI) |
| **Contracting Officer's Representative (COR)** | Dr. Richard T. Tischer<br>U.S. DOE, PETC, Pittsburgh |
| **Reporting Period:** | July 1, 1994 - September 30, 1994 |
| **Objectives:** | To carry out Mössbauer spectroscopy study of Iron-based catalysts used in FT synthesis to identify iron phases present and correlate with water gas shift and FT activities. |

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## Executive Summary

Mössbauer spectroscopy investigations were carried out on 7 iron-based catalysts during the period under review. A set of four samples subjected to activation in syn gas and Fischer-Tropsch synthesis were sent by R.J.Gormley, to understand the behavior of the low alpha catalyst used in these runs. Another three used catalyst samples extracted from the LaPorte Run II were sent By Dr.Bharat Bhatt to understand the phase distribution and any correlation with the run results. The high alpha UCI catalyst used in the LaPorte Run I in Aug.1992 was sent by Gormley at my request. This catalyst was studied to compare with the UCI low alpha catalyst used in LaPorte run II.

All together 10 Mössbauer measurements both at room and low temperatures were carried out to identify the iron phases present in these catalyst samples.

Although it is difficult to draw any definite conclusions from the data, some plausible trends are noticed as outlined below:

(1) Activation of the low alpha UCI catalyst in syn gas ($H_2$/CO) leads to the formation of about 50% of $Fe_3O_4$ and 36% of $Fe_5C_2$ ($\chi$-carbide) and the remaining being in the spm phase which is likely to be an oxide phase as revealed by other low temperature measurements.

(2) During FT synthesis, the $\chi$-carbide increases to 91 % in the sample with time on stream (TOS) value of 49 hrs.

(3) $Fe_3O_4$ decreases rapidly during FT synthesis from 49% to 7%

(4) The ($H_2$+CO) conversion for the 26hrs TOS sample (CW-S3-10-A) is only 16.6% and that of the 49 hrs TOS sample (CW-S3-10-B) is also low at 6.0%

(5) Decrease of $Fe_3O_4$ (magnetite) during FT synthesis indicates that water gas shift activity can be low. It is known that magnetite is active for WGS activity. Large amounts of water was found during the above runs confirming that the WGS activity was indeed low.

(6) Earlier Mössbauer measurements have shown that $Fe_5C_2$ ($\chi$-carbide) is active for FT synthesis. But in the present case, even though the catalyst contains as much as 91% $\chi$-carbide, the activity is very low at 6.0% for ($H_2$/CO) conversion. However there is a major difference between previous results and the present one. In the previous cases the $Fe_5C_2$ was formed more or less completely during activation itself and there was no further growth of the carbide during FT synthesis. On the contrary, in the present case the carbide is not fully formed during activation and it continues to grow even during FT synthesis. This may be a significant pointer which has to be further investigated to find if there is any inverse correlation between the growth of carbides during FT synthesis and the FT activity.

Summary of Technical Progress:

During the period under review only the scheduled Task 2 was carried out.

Mössbauer Spectroscopy Studies:

The U.S. Department of energy has currently a program to develop Fischer-Tropsch catalysts which are active at low $H_2/CO$ ratio of 0.7. Dr.Burt Davis, Dr.D.B.Bukur and R.J.Gormley have been developing Fischer-Tropsch catalysts which are active at a low $H_2/CO$ ratio. It is of interest to find out any relationships that may exist between the iron phases that are produced during activation and FT synthesis and the activity of the catalysts.

Mössbauer spectroscopy measurements of the following iron FT catalysts, received from :

(a) R.J. Gormley, PETC, DOE and (b) Dr Bharat Bhatt, Air Products Inc.

(a) Iron Catalysts received from R.J. Gormley:

| Sample | Description |
|---|---|
| UCI 1185-149-2ND | Fresh UCI catalyst (57.2%Fe/9.3%Cu/0.05%K)(all wt%) |
| CW-S3-10-ACT | Activated UCI 1185-149-2ND in C28 wax, activated in $H_2/CO$ @ 280°C for 14hrs, then sampled. |
| CW-S3-10-A | Ran UCI 1185-149-2ND in C28 wax, activated in $H_2/CO$ @ 280°C for 14hrs; run syn gas @ 270°C, 26hrs |
| CW-S3-10-B | Ran UCI 1185-149-2ND in C28 wax, activated in $H_2/CO$ @ 280°C for 14hrs; run syn gas @ 270°C, 49hrs |
| CW-S3-10-END-SETT | Same as above, but removed all hot catalyst/wax from reactor, let settle and sample out of the black portion. |

The results of analysis of Mössbauer spectra recorded are shown in Table I.

Table I

Spent catalysts from PETC, DOE

| Sample | TOS (HRS) | Spm Phase | $Fe_3O_4$ | $\chi$-$Fe_5C_2$ |
|---|---|---|---|---|
| CW-S3-10-ACT | 0 | 16 | 48 | 36 |
| CW-S3-10-A | 26 | 2 | 14 | 84 |
| CW-S3-10-B | 49 | 2 | 7 | 91 |
| S3-10-END-SETT | 49 | 18 | 8 | 74 |

Spm = Superparamagnetic

(b) Iron catalysts received from Dr Bharat Bhatt, Air Products Inc.

(1) FT run #2 (sample # 27.10)
Catalyst extracted from the reactor on May 16,1994

(2) FT run #2 (Sample ID No. 0900hrs)
Catalyst extracted from the reactor on June 2,1994

(3) FT run #2A (Drum #2,Catalyst L-3950 in Drekeol-10)
Catalyst extracted from the reactor on May 31,1994

The results of analysis of the room and low temperature Mössbauer spectra are given in Table II.

Table II
LaPorte run spent catalysts

| Sample | $Fe_3O_4$ | $\chi$-$Fe_5C_2$ |
|---|---|---|
| May 16,1994 | 64 | 36 |
| June 2,1994 | 16 | 84 |
| May 31,1994 | * | |

* Not yet analyzed due to shifting of laboratory.

As can be seen from the above table, there is a significant difference between the phases found in the May 16th and June 2nd spent catalysts. The May 16th sample belongs to the FT run that was terminated on May 13th as the catalyst completely lost its activity. The June 2 nd sample was extracted at the end of the successful FT run #2. This catalyst consists of 84% of $\chi$-$Fe_5C_2$ which is believed to be a possible active phase for the FT synthesis.