FINAL

DOE/PC/93066--T2

QUARTERLY TECHNICAL PROGRESS REPORT

(April-June, 1994)

CONTRACT TITLE:	MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES
Contract Number:	DE-AC22-93PC93066
	University of Kentucky, Lexington, KY
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Contracting Officer's Representative (COR)	Dr. Richard T. Tischer U.S. DOE, PETC, Pittsburgh
Reporting Period:	April 1, 1994 - June 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 16 iron-based catalysts during the period under review. A set of 10 samples subjected to different pretreatments and Fischer-Tropsch synthesis were sent by Prof. D.B. Bukur, to understand the effect of reduction in different gas atmospheres on the iron phases formed. Another set of 5 catalysts pretreated in CO and subjected to Fischer-Tropsch synthesis using two kinds of wax viz., (a) a low molecular wt. wax and (b) heavy wax were sent by R.J.Gormley. As prepared UCI-1185-149-2ND which was used in the FT studies also sent for Mössbauer characterization.

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

(1) Pretreatment of a catalyst in H_2 leads to the formation of ε-carbide.
(2) Pretreatment of a catalyst in H_2/CO leads to the formation of χ-carbide.
(3) Reduction o UCI-1185-149-2ND catalyst in CO leads to the formation of χ-carbide.
(4) Reduction of DOE catalysts in CO leads to the formation of ε-carbide.

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.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) from Prof. D.B.Bukur, Texas A & M University, College Station, TX. were carried out.

(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%)
S3-08-END-SETT	UCI 1185-149-2ND in C28 wax, activated in CO @ 270°C for 24hrs, run syngas @ 270°C (57.2%Fe/9.3%Cu/0.05%K)(all wt%)
S3-07-END-SETT	UCI 1185-149-2ND in Allied wax, activated in CO @ 270°C for 24hrs, run syngas @ 270°C (57.2%Fe/9.3%Cu/0.05%K)(all wt%)
S3-04-END-SETT	MB6-ABC-1-81 in C28 wax, activated in CO @ 280°C for 21.5hrs,run syngas @ 255°C (65.8%Fe/2.9%Cu/0.3%K)(all wt%)
S1-109-END-SETT	MB6-ABC-1-81 in C28 wax, cativated in CO @ 280°C for 24.0hrs,run syngas @ 255°C, 383hrs. (65.8%Fe/2.9%Cu/0.3%K)(all wt%)
S3-09-END	UCI 1185-149-2ND in C28 wax, activated in He/CO @ 270°C for 10.0hrs, run syngas @ 270°C (57.2%Fe/9.3%Cu/0.05%K)(all wt%)

(b) Spent Slurry Iron Catalysts with the following composition: withdrawn at various times on stream: (Received from DR.D.B.Bukur)

100Fe/5%Cu/4.2%K/16SiO_2
(All wt%)

Gormley activated his catalysts in CO or He/CO. Some of his catalyst have given rise to good FT conversions and some lost their activity in relatively short time. He wanted to know the nature of the iron phases formed in two types of catalysts and seek any relationships could be established between the iron phases and the FT activity. He has used two types of catalysts in his FT runs viz., (a) UCI 1185-149 2ND (57.2%Fe /9.3%Cu/0.05%K) and (b) DOE catalyst (65.8%Fe/2.9%Cu/0.3%K). They were activated in CO or He/CO. The present investigations have shown that the UCI catalyst gave rise to preferentially to χ-Fe_5C_2 while the DOE catalysts to ε-$Fe_{2.2}C$. The iron phases found in the catalysts are shown in the Table I.

Table I
R.J.Gormley
PETC, DOE

Run#	CFFLS #	Sample	Spm Phase	Fe_3O_4	χ-Fe_5C_2	ε-$Fe_{2.2C}$
1844	1225	S3-08-END-SETT	14	11	75	
1845	1226	S3-07-END-SETT	16	60	24	
1846	1227	S3-04-END-SETT	14	29	9	48
1849	1228	UCI-1185-149-2ND	100 Bulk α-Fe_2O_3			
1847	1229	S1-109-END-S	19	20	9	52
1848	1230	S3-09-END	13	35	52	

Spm = Superparamagnetic

Dr.Bukur has activated the catalysts in H_2 or H_2 /CO and wanted to know the iron phase distribution in the catalysts formed during the FT synthesis at various time on stream values. The present Mössbauer investigations have shown that activation of the catalyst 100Fe/5Cu/4.2K/16SiO_2 in H_2 leads to the formation of ε-$Fe_{2.2}C$ while activation in H2/CO leads to χ-Fe_5C_2. The iron phases found in the catalysts at various times on stream are shown in the Table II.

Table II

Prof.D.B. BUKUR
Slurry Samples

MK#	CFFLS#	Sample	Spm	α-Fe	Fe_3O_4	χ-Fe_5C_2	ε-$Fe_{2.2}C$
1560	1053	SB-0802 TOS=166	4	26	15	9	45
1622	1054	SB-1421 TOS=0	100				
1558	1055	SB-1421 TOS=665	56				44
1561	1056	SB-1421 TOS=667	60				40
1620	1057	SB-1421 TOS=EOR	76				24
1628	1058	SA-2862 TOS=0	44		29	27	
1576	1059	SA-2862 TOS=223	39		34	27	
1630	1060	SA-2862 TOS=227	45		29	26	
1559	1061	SA-2862 TOS=EOR	32		31	37	
1626	1062	SB-2932 TOS=EOR	35		43	8	14