FINAL - APPROVED

DOE/PC/93066--T6

QUARTERLY TECHNICAL PROGRESS REPORT

(April-June, 1995)

CONTRACT TITLE:	MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES
Contract Number:	DE-AC22-94PC93066
	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 U.S. DOE, PETC, Pittsburgh
Principal Investigators:	Prof. Gerald P. Huffman, (PI) Dr. K.R.P.M.Rao, (Co-PI)
Contracting Officer's: Representative (COR)	Dr. Richard T. Tischer U.S. DOE, PETC, Pittsburgh
Reporting Period:	April 1, 1995 - June 30, 1995
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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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. Robert J. Gormley (PETC/DOE) has 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 investigations were carried out on 10 iron-based catalysts during the period under review. The catalysts UCI 1185-149 (2nd & 3rd) 57.2Fe/9.3Cu/0.05K (all atomic ratios) were subjected to activation in CO gas atmosphere. Fischer-Tropsch (FT) synthesis was carried out with 9 wt% catalyst (obtained from 2nd batch) and 23 wt% catalyst (obtained from 3rd batch) in Petrolite 655 (a heavy wax) to understand the effect of different loadings in the wax medium on the phase distribution and its effect on the FT activity. These samples were sent by Robert J. Gormley.

The following trends were observed:

(1) Activation of the catalyst UCI 1185-149 (from the 2nd batch) in CO for 22hrs lead to the formation of 81% of χ-Fe_5C_2 besides Fe_3O_4 and superparamagnetic phase which is likely to be α-FeOOH.

When 9 wt% of the catalyst in the heavy wax medium was subjected to FT synthesis the activity was initially good at about 88% of (H_2+CO) conversion but subsequently deactivated to 66% at TOS=281hrs.

(2) Activation of the catalyst UCI 1185-149 (from the 3rd batch) in CO for 22hrs lead to the formation of 87.5 % of χ-carbide besides Fe_3O_4 and superparamagnetic phase which is likely to be α-FeOOH.

When 23 wt% of the catalyst in the heavy wax medium was subjected to FT synthesis the activity was initially good at about 86% of (H_2+CO) conversion.

The amount of the catalyst used in the two cases did not make any difference in the formation of the chi-carbide. In both the cases good amount of chi-carbide was formed and the initial FT activity was good..

Summary of Technical Progress:

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

Mössbauer spectroscopy measurements of the following 10 iron catalysts received from Robert J. Gormley, PETC, Department of Energy, were carried out. The catalysts were subjected to Mössbauer measurements as received without any cleaning of any wax coating present on the surface of the catalysts.

Results:

The UCI 1185-149 (57.2Fe/9.3Cu/0.05K) catalyst gets converted to χ-Fe_5C_2 to the extent of about 80-85% when activated in CO atmosphere in both the cases of loading. During FT synthesis the chi-carbide gets converted to magnetite,Fe_3O_3 and a superparamagnetic phase of an oxide, which is most likely geothite,α-FeOOH as per the low temperature measurements made earlier on similar samples. The initial FT activity is high at 80-85% of (H_2+CO) conersion. The trend observed in the present measurements is consistant with the earlier observation that the carbides formed during activation are conducive for good FT activity as against the carbides which are formed during FT synthesis which lead to poor FT activity.

The amount of the catalyst used did not make any difference in the formation of chi-carbide, χ-Fe_5C_2 or the initial FT activity.

The phase distributions observed in the case of 9 wt% loading and 23 wt% loading are shown in Tables I and II.

Table I

Conditions of activation and FT synthesis are given below

Catalyst: 9% UCI 1185-149 (57Fe/9.3Cu/0.05K) from 2nd batch
CO-activated: for 22hrs at 270°C, 175psig, 1.4nL of CO /hr/g Fe
FT synthesis: At 270°C, 175psig, 2.4nL of syngas /hr/g Fe, at 100rpm.in Petrolite Polywax 655, a heavy wax.

9 wt% catalyst loading

Sample@	χ-Fe_5C_2	Fe_3O_4	Spm phase	% (H_2+CO) conversion *
Activated for 22hrs	81	13	6	----
FT run TOS=116hrs	50	26	24	87.5
FT run TOS=140hrs	53	27	22	86.9
FT run TOS=281hrs	61	24	15	65.8

* Catalyst preparation and FT runs were carried out at PETC / U.S.D.O.E.

Table II

Conditions of activation and FT synthesis are given below

Catal;yst: 23% UCI 1185-149 (57Fe/9.3Cu/0.05K) from 3rd batch
CO-activated: for 22hrs at 270°C, 175psig, 1.4nL of CO /hr/g Fe
FT synthesis: At 270°C, 175psig, 2.4nL of syngas /hr/g Fe, at 100rpm.in Petrolite Polywax 655, a heavy wax.

23 wt% catalyst loading

Sample@	χ-Fe_5C_2	Fe_3O_4	Spm phase	$\acute{\varepsilon}$-$Fe_{2.2}C$	% (H_2+CO) Conversion*
Activated for 2 hr	--	78	10	12	--
Activated for 18hr	63	33	4	-	--
Activated for 220hr	87	9	4	-	--
FT run TOS=21hr	65	15	20	-	86.0
FT run TOS=43hr	54	22	24	-	75.4
FT run TOS=92hr	51	25	24	-	85.0

* Catalyst preparation and FT runs were carried out at PETC/ U.S.D.O.E.