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QUARTERLY TECHNICAL PROGRESS REPORT
(October-December, 1995)

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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 1995)
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:	October 1, 1995 - December 31, 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. Dr. Burtron Davis of University of Kentucky 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 16 iron-based catalysts during the period under review. Mössbauer measurements on two of the samples were also carried out at 13.5°K. The composition of one set of the catalysts studied consists of 100Fe/3.6Si/0.71K (all atomic % relative to Fe). Activation was carried out in syngas at a low pressure of 1 atm to investigate the effect of low pressure activation as compared to high pressure activation. The composition of a second set of catalysts consisted of 100Fe/3.6Si/2.6Cu/0.71K (all atomic % relative to Fe) and activation was carried out in syngas at a relatively high pressure of 12 atm. The composition of a third set of catalysts consisted of 100Fe/4.4Si/2.6Cu/1.0K (all atomic % relative to Fe) and activation was carried out in H_2 at 1 atm. In all the cases the temperature was kept at 270°C and space velocity at 3.3nL/hr-g(Fe) for 24hrs. Fischer-Tropsch (FT) synthesis was carried out at 13 atm at 270°C, 3.4nL/hr-g(Fe) syngas/g-Fe/ hrs

These samples were provided by Dr. Burtron Davis, University of Kentucky.

RESULTS:

The phase distributions observed are shown in Tables I, II and III respectively for the catalysts activated in syngas at (i) low pressure of 1 atm and (ii) high pressure of 12 atm and for the catalysts activated in H_2 at 1 atm.

The Mössbauer results indicate that the activation of the catalysts in syngas at a low pressure of 1 atm gives rise to the formation of 41% of chi-carbide, χ-Fe_5C_2 (in addition to magnetite and superparamagnetic oxide) during activation period as compared to zero carbide observed when the catalyst was activated in syngas at a high pressure of 12 atm. Activation in H_2 results in the formation of iron metal during activation and epsilon' carbide, $\acute{\epsilon}$-$Fe_{2.2}C$ during FT synthesis period.

It is significant to note that activation in syngas at low pressure of 1 atm leads to the formation of chi-carbide while activation at high pressure of 12 atm does not lead to the formation of any chi-carbide. Earlier studies (DOE Contractors Review meeting, August 1995, Pittsburgh) have shown that the presence of chi-carbide is conducive for good FT conversion and further, that the carbides formed during activation give rise to good FT activity. In the present case, one would expect good FT activity for the catalysts activated in syngas at low pressure as compared to the catalysts activated at a higher pressure. The (H_2+CO) conversion of the catalyst activated at 1 atm was found to be 82% while the conversion of the catalyst activated at 12 atm was only about 50% consistent with the general trends observed earlier. Although the FT activity of syngas activated (at 1 atm) catalyst is 82% (H_2+CO) conversion at the beginning of the FT run, later it gets deactivated with time to about 69%. The amount of chi-carbide formed at the end of 24hr syngas activation was 41% and it decreased to 20% after 384hrs of FT run.

The low temperature measurement has indicated that the Spm phase observed at room temperature consists of an iron oxide and not any carbide phase.

Summary of Technical Progress:

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

Mössbauer spectroscopy measurements on 16 iron catalysts received from Dr. Burtron Davis, University of Kentucky 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. Low temperature measurement was made on two of the samples to identify the nature of the superparamagnetic phase.

Table I

Pretreatment Carried out at Low Pressure (1 atm)

Conditions of activation and FT synthesis are given below:

Catalyst: 100Fe/3.6Si/0.71K (atomic % relative to Fe)
Activation conditions: 270°C, 1atm , $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe),24hrs
Synthesis conditions: 270°C, 13 atm, $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe)

Sample	χ-Fe_5C_2	Fe_3O_4	Spm phase	% (H_2+CO) conversion*
Activated for 24hrs	41	32	27	----
FT run TOS=24hrs	36	40	24	82.0
FT run TOS=48hrs	31	47	22	83.0
FT run TOS=95hrs	33	48	19	79.0
FT run TOS=218hrs	26	50	24	75.0
FT run TOS=384hrs	20	60	20	69.0

* Catalyst preparation and FT synthesis was carried out at CAER, UK

Table II

Pretreatment Carried out at High Pressure (12 atm)

Conditions of activation and FT synthesis are given below:

Catalyst: 100Fe/3.6Si/2.6Cu/0.71K (atomic % relative to Fe)
Activation conditions: 270°C, 12 atm, $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe),24hrs
Synthesis conditions: 270°C, 13 atm, $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe)

Sample	χ-Fe_5C_2	Fe_3O_4	Spm phase	% (H_2+CO) conversion *
FT run for 4.33hrs	--	81	19	26.0
FT run TOS=21hrs	--	90	10	26.0
FT run TOS=45hrs	--	86	14	32.0
FT run TOS=113.7hrs	15	82	3	43.0
FT run TOS=214.5hrs	20	76	4	51.0

Table III

Conditions of activation and FT synthesis are given below:

100Fe/4.4Si/2.6Cu/1.0K (atomic ratio relative to Fe)
Activation in H_2 at 220°C, 1atm, 2000cc/min, 24h
Synthesis conditions: 270°C, 13atm, 3.4nL/hr-g(Fe), $H_2/CO=0.7$

Catalyst	Spm-phase	Fe_3O_4	Fe-metal	$\acute{\varepsilon}\text{-}Fe_5C_2$	%Conv. (H_2+CO)
RJO-189A 2hr,15min Pre-treatment	80	20	--	--	--
RJO-189B 4hr 25min Pre-treatment	42	58	--	--	--
RJO-189C 12h 24min Pretreatment	18	72	10	--	--
RJO-189D 26hr 30min Pre-treatment	11	65	24	--	--
RJO-189E TOS=3h synthesis	8	62	4	26	76