TITLE: MÖSSBAUER STUDY OF IRON-CARBIDE GROWTH AND FISCHER-TROPSCH ACTIVITY

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OBJECTIVE: The objective of the project is to develop an understanding of the catalytic conversion of synthesis gas into liquid products through a determination of the phases, structure, and particle-size distributions of the iron-based catalysts, as measured by Mössbauer and XAFS spectroscopies. Relationships that exist between process conditions and the iron-bearing phases in the catalyst are investigated in the present studies.

ACCOMPLISHMENTS AND CONCLUSIONS: The present studies indicate that the presence of carbides is essential but not a sufficient condition for good FT activity. It is shown that the nature of growth of carbides during pretreatment and FT synthesis is correlated with the FT activity.It is also shown that the pressure at which the catalyst is activated affects the carbide phase formation. The liquid medium used for the FT synthesis is shown to alter the phase distribution. Heavy wax medium gave rise to less carbide as compared to light wax medium.

ABSTRACT: There is a need to establish a correlation between the Fischer-Tropsch (FT) activity of an iron-based catalyst and the catalyst phase during FT synthesis. The nature of iron phases formed during activation and FT synthesis is influenced by the nature of the gas and pressure apart from other parameters like temperature, flow rate etc., used for activation. Mössbauer investigations of iron-based catalysts subjected to pretreatment at two different pressures in gas atmospheres containing mixtures of CO, H_2, and He have been carried out. Studies on UCI 1185-57 (64%Fe_2O_3/5%CuO/1%K_2O/30% Kaolin) catalyst indicate that activation of the catalyst in CO at 12 atms. leads to the formation of 100% magnetite and the magnetite formed gets rapidly converted to at least 90% of χ-Fe_5C_2 during activation. The FT activity was found to be good at 70-80% of (H_2+CO) conversion. On the other hand, activation of the catalyst in synthesis gas at 12 atms. leads to formation of Fe_3O_4 and it gets sluggishly converted to χ-Fe_5C_2 and $\acute{\epsilon}$-$Fe_{22}C$ during activation and both continue to grow slowly during FT synthesis. FT activity is found to be poor.

Pretreatment of the catalyst, 100Fe/3.6Si/0.71K at a low pressure of 1 atms. in syngas gave rise to the formation of χ -Fe_5C_2 and good FT activity. On the other hand, pretreatment of the catalyst, 100Fe/3.6Si/0.71K at a relatively high pressure of 12 atms. in syngas did not give rise to the formation any carbide and FT activity was poor.

INTRODUCTION: Pretreatment of iron catalysts is an important step in the development of an efficient catalyst. It affects the distribution of iron phases that are formed during the pretreatment and changes that take place during synthesis. It is controlled by the type of gas, temperature (T), pressure (P) and gas space velocity (S.V.) used. The FT activity and possibly selectivity are related to the iron phases present in the catalyst; however the role of any specific phase on the FT synthesis is not yet clearly understood.

Mössbauer characterization of two iron based catalysts, viz., UCI 1185-57 (64%Fe_2O_3/5%CuO/1%K_2O/30% Kaolin) and UCI 1185-149 (57.2Fe/9.3Cu/0.05K) has been carried out with a view to identify and quantify the different iron phases that are present in the activated and spent catalysts and study their influence on Fischer-Tropsch (FT) synthesis. The catalysts were activated in (i) CO and (ii) H_2/CO (syngas) and then subjected to FT synthesis.

EXPERIMENTAL:

(I) ASSOCIATION OF CARBIDE PHASE WITH FT ACTIVITY

CO-ACTIVATED UCI 1185-57 CATALYST: The UCI 1185-57 catalyst (64%Fe_2O_3/5%CuO/1%K_2O/30% Kaolin) was ramped to 270°C @1.5°C/min under CO atmosphere at 175psig and maintained at 270°C in CO for 24hrs with a flow rate of 2.0nL/hr/g-Fe at 175psig. It was then subjected to FT run with a syngas of H_2/CO=0.7 at 270°C, with a space velocity=3.4nL/hr/g-Fe at 175psig. The catalyst samples were withdrawn at various times during pretreatment and FT synthesis. The phase distribution determined is shown in Fig.1. The phases formed consist of magnetite, chi-carbide and a superparamagnetic phase (spm phase) which is an oxide. χ-Fe_5C_2 phase, to the extent of 90%, is formed rapidly during the 24hrs of activation in CO.

SYNGAS-ACTIVATED UCI-1185-57 CATALYST: The UCI 1185-57 catalyst was preheated in He up to 200°C at 2.0°C/min at 150psig and then to 280°C, at 7.0°C/min. and held for 12hrs. The FT synthesis was carried out in (H_2+CO)=0.7 with a flow rate of 2.5nL/hr/g-Fe at 265°C and 200psig. The catalyst samples were withdrawn at various times during pretreatment and FT synthesis. The phase distribution determined is given in shown in Fig.2. As compared to the CO pretreatment, activation in synthesis gas, leads to slow growth of χ-carbide and $\acute{\varepsilon}$-carbide at the expense of Fe_3O_4. The carbides are formed in proportion to the pretreatment and synthesis duration in addition to magnetite, some substituted magnetite and a small fraction of superparamagnetic phase which is an iron oxide.

The hematite is converted into magnetite (Fe_3O_4) during heating the catalyst in CO up to 270°C in 2hrs 43 min. The magnetite is rapidly converted into χ-Fe_5C_2 during further pretreatment under CO at 270°C and 175psig. The conversion is 90 % at the end of 24hrs of pretreatment. The remaining 10 % of magnetite is converted into superparamagnetic (spm) phase. Low temperature (12°C) measurement on one of the used catalyst has revealed that the spm phase is magnetite. During FT synthesis part of the χ-Fe_5C_2 (~25%) gets converted back to Fe_3O_4 and spm phase, possibly due to oxidation by the water generated during WGS reaction. However, after about 20 hrs of FT synthesis χ-Fe_5C_2, Fe_3O_4 and the spm phase reach equilibrium values. The FT activity is also maintained at an equilibrium value of ≈70% (H_2+CO) conversion.

It was found that the activity of the catalyst was better when activated in CO than in synthesis gas. As compared to the CO pretreatment, the synthesis gas pretreatment leads to a slow growth rate of χ-Fe_5C_2 and $\acute{\varepsilon}$-$Fe_{2.2}C$ at the expense of Fe_3O_4 and ≈ 30% (H_2+CO) conversion at the end of 24 hrs of activation. The χ-Fe_5C_2 and $\acute{\varepsilon}$-$Fe_{2.2}C$ continue to grow during FT synthesis while Fe_3O_4 continues to decrease indicating that magnetite is getting converted into carbides, a trend which is opposite to that seen in the case of CO-activated catalyst as shown in

Fig.1 where the total carbide formed is plotted. It may be noted that there is no ε-$Fe_{2.2}C$ formed during either pretreatment or FT synthesis in the present case of CO pretreated catalysts.

The variation of the ($CO+H_2$) conversion for the two types of pretreatment is shown in Fig. 3. The ($CO+H_2$) conversion is maintained at ≈70% in the case of CO pretreated catalyst when the χ-Fe_5C_2 is maintained at ≈65% and the magnetite at 35%. On the other hand, in the case of synthesis gas pretreated catalyst, the conversion is ≈ 60% during activation for a relatively short time and drops to ≈ 30% at the start of FT run and continues to be low. The carbides were formed during activation and continue to grow throughout FT run at the expense of magnetite. The growth of carbides even during FT synthesis might imply that reduction of the catalyst is not complete during activation in synthesis gas.

The rapid formation of the carbide in the case of CO pretreated catalyst may possibly imply that the surface of the catalyst is clean and that the CO gas is able to penetrate the catalytic surface and give rise to the rapid formation of the carbide and FT activity. On the other hand, sluggish formation of the carbides in the case of syngas pretreated catalyst might imply that the catalytic surface is covered with some inactive or graphitic carbon which slows down the formation of carbides and diminishes the FT activity.

We have also carried out Mössbauer investigations on the low α catalyst, UCI 1185-149, 57.2Fe/9.3Cu/0.05K (from 2nd and 3rd batch) subjected to pretreatment in (i) CO and (ii) H_2/CO. The pretreatment and FT synthesis conditions and the phase distribution determined are given in Tables I to II.

CO-ACTIVATED UCI 1185-149 (2nd batch) (57.2Fe/9.3Cu/0.05K):

UCI 1185-149 (2nd batch) catalyst was pretreated in CO at 270°C, 175 psig, for 22hrs in 1.4 nL CO/g-Fe hr. FT synthesis was carried out in distilled Allied-Signal heavy wax with 9% catalyst loading at 270°C, 175psig, 2.4 nL syngas/g-Fe hr, at 1000rpm.

The activation is not complete during pretreatment. As can be observed from the Table I, the χ-carbide continues to grow during FT synthesis and the FT activity which was initially high at 84% of (H_2+CO) conversion decreases rapidly with increasing time on stream. This might imply the presence of some inactive or graphitic carbon on the surface of the catalyst.

SYNGAS-ACTIVATED UCI 1185-149 (2nd batch) (57.2Fe/9.3Cu/0.05K): UCI 1185-149 (2nd batch) catalyst was pretreated in H_2/CO at 280°C, 175 psig, for 14hrs in 1.4 nL CO/g-Fe hr. FT synthesis was carried out in C28 wax with 9% catalyst loading at 270°C, 175psig, 2.4 nL syngas/g-Fe hr, at 1000rpm. In this case also the activation is not complete during pretreatment. As can be observed from the Table II, the χ-carbide continues to grow during FT synthesis and the FT activity which was initially low decreases still further with increasing time on stream. It may be noted that the FT activity is low even when the χ-Fe_5C_2 present in the spent catalyst is as much as 91%. This indicates that the absolute amount of χ-Fe_5C_2 present in the catalyst may not be significant for FT activity. The slow growth of carbide observed might imply the possible deposition of some inactive carbon on the surface.

(II) INFLUENCE OF LIQUID MEDIUM ON THE CARBIDE PHASE FORMATION:

The UCI 1185-149 (3rd batch) catalyst under the same conditions of activation and FT synthesis except for the liquid medium used gave rise to different amounts of carbide depending up on the nature of the medium. Lighter wax gave relatively larger amounts of chi-carbide compared to the heavier wax during FT synthesis as shown in Tables III and IV. Although the initial activity is high in both the cases, the deactivation is rapid in the case of the catalyst containing lesser amount of carbide.

(III) INFLUENCE OF PRESSURE USED FOR ACTIVATION:

SYNGAS ACTIVATION OF AN IRON CATALYST AT LOW PRESSURE VS HIGH PRESSURE:

The pressure at which an iron catalyst is activated in syngas has a profound effect on the phase distribution and consequently on the FT activity. When the catalyst 100Fe/3.6Si/0.71K (atomic ratio) was activated in syngas at 12 atms for 24hrs @ 270°C, 3.4nL/hr-g(Fe), $H_2/CO=0.7$ no carbide was formed even when the activation was continued for 93 hrs. as shown in Table V. However, activation of the the same catalyst in CO (after 93hrs. of activation in syngas) only for 22hrs leads to the formation of 33% of χ-carbide and the FT activity increased to about 88% at TOS=77.5hrs. The FT activity does not correlate with the bulk carbide present.

Adding Cu to the catalyst did not improve carbide formation under similar activation conditions as can be seen from Table VI. The FT activity was low at about 10% of (H_2+CO) conversion at the end of 24 hrs of TOS.

Activation of 100Fe/3.6Si/0.71K (atomic ratio) in syngas at 1 atms gave rise to 41% of χ-carbide and the FT activity of the catalyst was high at about 85% of (H_2+CO) conversion at the end of 24hrs of TOS as shown in Table VII.

CONCLUSIONS: It is shown that the presence of χ-carbide in a catalyst is essential for good FT conversion but may not be a sufficient condition.. It may not be the amount of χ-carbide that is significant but the formation of the carbide during activation period seems to be important for good FT activity. The above results imply a correlation between the growth rate of carbide formed during activation and the FT activity. Rapid and complete formation of χ-Fe_5C_2 during activation may indicate that the catalyst surface is clean and conducive for good FT activity. Large amounts of χ-Fe_5C_2 present in spent catalysts may not necessarily indicate good FT conversion as has been observed in the present Mössbauer studies.

It is observed that in the case of CO activation the carbide content increases during activation and decreases during FT synthesis resulting in good FT activity. On the other hand in the case of syngas activation under high pressure the carbide formation is slow and incomplete during activation and continues to grow during synthesis resulting in poor FT activity. Activation in syngas at low pressure gives rise to χ-Fe_5C_2 during activation and decreasing amounts of χ-Fe_5C_2 during FT synthesis leading to good FT activity.

It is possible that the active surface species form only under conditions that are also favor bulk carbide formation. The FT activity results suggest that this surface is more stable than the bulk carbide.

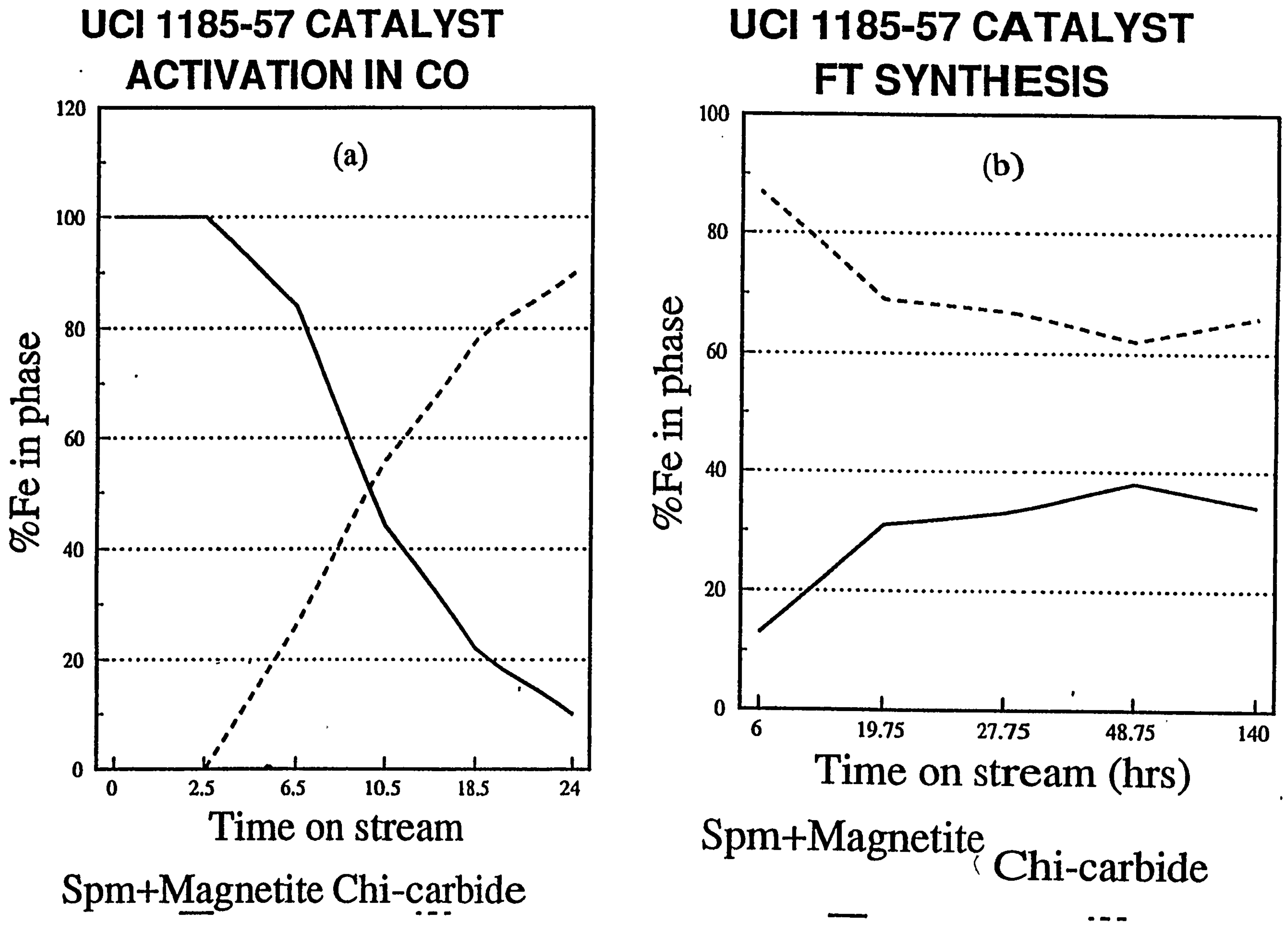

Fig. 1 Iron phase distribution in the catalyst UCI 1185-57 vs TOS
(a) during activation in CO and (b) during FT synthesis

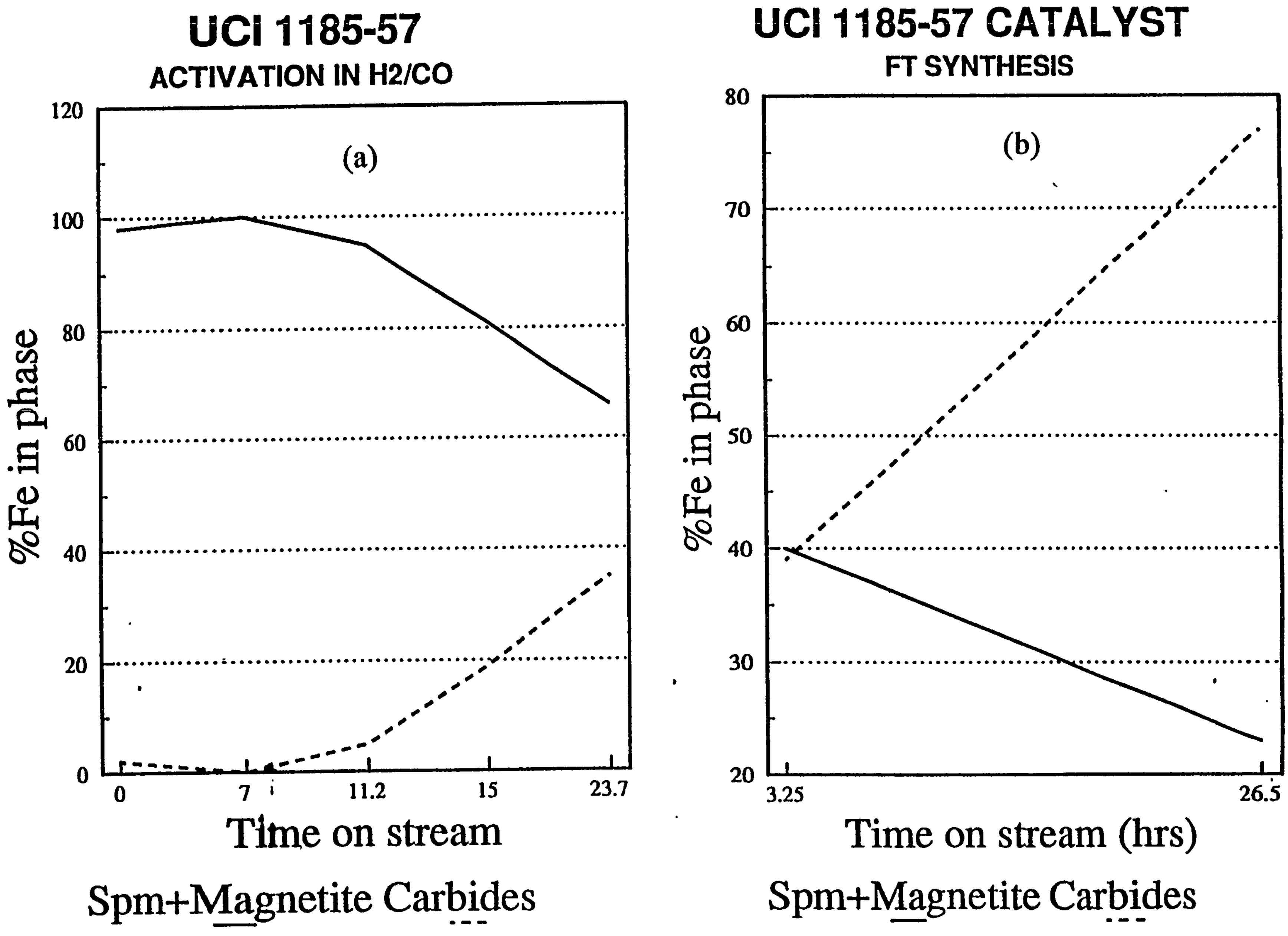

Fig.2 Iron phase distribution in the catalyst UCI 1185-57 vs TOS
(a) during activation in syngas and (b) during FT synthesis

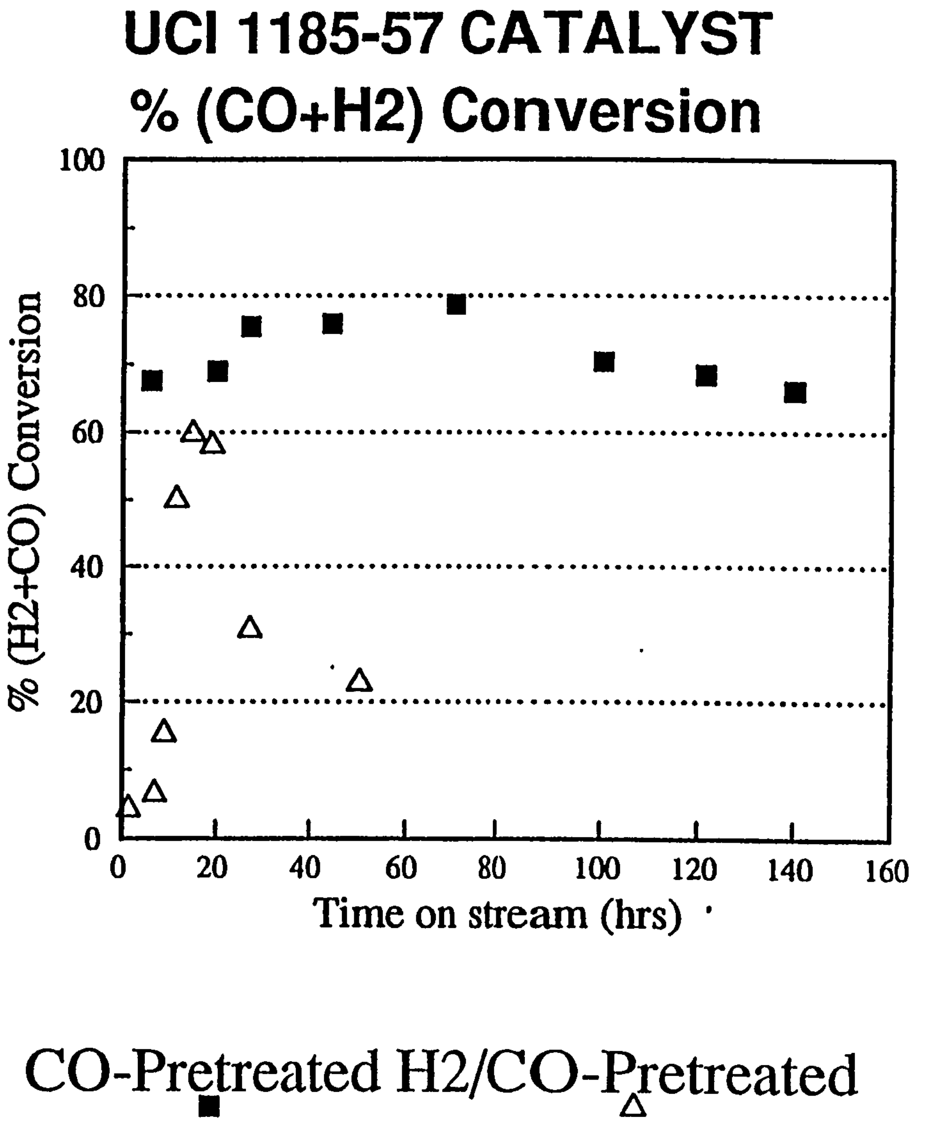

Fig.3 (H2+CO) conversion dependance on pretreatment

Table I

Catalyst: UCI 1185-149-2nd (57.2Fe/9.3Cu/0.05K)
Activated in CO at 270°C, 175psig,22hr, 1.4nL/hr-gFe
FT synthesis conditions: $H_2/CO=0.70$, 270°C, 175psig,2.4nL/hr-gFe
9% catalyst loading in distilled Allied-Signal heavy wax of 370gms.

SAMPLE	χ-Fe_5C_2	Fe_3O_4	Spm	(H 2+CO) Conversion %*
FT run TOS=84hrs	40	37	23	84.0
FT run TOS=235hr	60	30	10	67.7
FT run TOS=305hr	68	27	5	51.2

* Catalyst preparation and FT synthesis runs were carried out at PETC, Pittsburgh

In the case of CO activation, increasing carbide content during FT synthesis gives rise to decreasing FT activity as can be seen from the above table.

Table II

Catalyst: UCI 1185-149-2nd (57.2Fe/9.3Cu/0.05K)
Activated in syngas at 270°C, 175psig,22hr, 1.4nL/hr-gFe
FT synthesis conditions: $H_2/CO=0.70$, 270°C, 175psig,2.4nL/hr-gFe
9% catalyst loading in C-28 light wax of 370gms.

Sample	χ-Fe_5C_2	Fe_3O_4	Spm phase	(H2+CO)* conversion
Activated for 14hrs	36	48	16	--
FT run TOS=26hrs	84	14	2	16
FT run TOS=9hrs	91	7	2	6

* Catalyst preparation and FT runs were carried out at PETC,Pittsburgh

In the case of syngas pretreatment, increasing carbide content during synthesis gave rise to low FT activity as can be seen from the above table.

Table III

Catalyst: UCI 1185-149-3rd ((57.2Fe/9.3Cu/0.05K):
Activated in CO at 270°C, 175psig,22hr, 1.4nL/hr-gFT

9% loading in C28, n-octacosane, light wax of 370gms.
Synthesis conditions: H_2/CO=0.70, 270°C, 175psig,2.4nL/hr-gFe

FT synthesis in light wax

Sample@	χ-Fe_5C_2	Fe_3O_4	Spm phase	ϵ-$Fe_{2.2}C$	%(H_2+CO) conversion*
Activated for 2hr	---	82	6	12	--
Activated for 18hr	77	21	2	---	--
Activated for 22 hr	86	12	2	---	--
FT run TOS=19.5	58	15	27	---	89
FT run TOS=43 hr	56	16	28	---	91
FT runTOS=90 hr	65	20	15	---	91
FT runTOS=160 hr	56	21	23	---	91

Table IV

FT synthesis in a heavy wax

Catalyst: UCI 1185-149-3rd ((57.2Fe/9.3Cu/0.05K): 9% loading in distilled Allied-Signal wax of 370gms.
Activated in CO at 270°C, 175psig,22hr, 1.4nL/hr-g
FT synthesis conditions: $H_2/CO=0.70$, 270°C, 175psig,2.4nL/hr-gFe

Sample	χ-Fe_5C_2	Fe_3O_4	Spm phase*	ϵ-$Fe_{2.2}C$	% (H_2+CO) conversion *
Activation for 2hrs	---	88	6	6	--
Activation for 9.5h	54	37	9	----	--
Activation for 22h	64	27	9	---	--
FT run TOS=24h	42	30	28	---	81
FT runTOS=47.5h	39	34	27	---	48
FT run TOS=94.5h	37	40	23	---	86

*The Spm phase i.e. superparamagnetic phase is likely to be α-FeOOH as revealed by low temperature measurements on UCI 1185-149-3rd catalyst subjected to CO activation and 24hrs of FT synthesis.

Table V

Activation carried out at high pressure (12 atms):

Catalyst: 100Fe/3.6Si/0.71K (atomic % relative to Fe)

Initial Activation in syngas at 12 atms, 270°C, $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe)

Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), $H_2/CO=0.7$

Catalyst	Spm-phase	Fe_3O_4	χ-Fe_5C_2	% Conversion*
Syngas:TOS=6.33h	75	25	-	9.2
Syngas:TOS=24.0h	31	69	-	9.7
Syngas:TOS=46.0h	11	89	-	11.5
Syngas:TOS=93.0h	-	100	-	12.2
CO: TOS=22.0h	9	58	33	25
Syngas:TOS=26.5h	15	60	25	59
Syngas:TOS=77.5h	18	63	19	88
Syngas:TOS=198.0h	13	67	20	86
Syngas:TOS=341.0h	11	63	26	81

*Catalyst preparation and FT runs were carried out at CAER, University of Kentucky

Table VI

Pretreatment carried out at high pressure (12 atms):

100Fe/3.6Si/2.6Cu/0.71K (atomic % relative to Fe)
Activation in Syngas at high pressure (12 atms): 270°C, $H_2/CO=0.7$; S.V.=3.4 nL/hr/g(Fe),24hrs
Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), $H_2/CO=0.7$

Catalyst	Spm-phase	Fe_3O_4	χ-Fe_5C_2	% (H_2+CO) Conversion✱
TOS=4.33h	19	81	-	26
TOS=21.0h	10	90	-	26
TOS=45.0h	14	86	-	32
TOS=113.7h	3	82	15	43
TOS=214.5h	4	76	20	51

✱Catalyst preparation and FT runs were carried out at:
CAER, University of Kentucky

Table VII

<u>Pretreatment carried out at low pressure (1 atms):</u>
Catalyst: 100Fe/3.6Si/0.71K (atomic % relative to Fe)
Activation conditions: 270°C, 1 atm., $H_2/CO=0.7$, S.V.=3.4 nL/hr/g(Fe),24hrs
Syntheisis 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
FT run TOS=218hrs	26	50	24	75
FT run TOS=384hrs	20	60	20	69