

### **3.2.3 MÖSSBAUER STUDY OF IRON FISCHER-TROPSCH CATALYSTS DURING PRETREATMENT AND SYNTHESIS**

#### **ABSTRACT**

Mössbauer data indicate that pretreating an iron Fischer-Tropsch catalyst containing Cu, K and Kaolin with syngas for 24 hours at 270°C and 12.9 atm. produces a material that has essentially all of the iron in the form of  $\text{Fe}_3\text{O}_4$ ; on the other hand, following a similar pretreatment except CO is substituted for the syngas produces a material that contains more than 80% of the iron in the form of  $\chi\text{-Fe}_{2.2}\text{C}$  and the remainder as  $\text{Fe}_3\text{O}_4$ . The CO pretreated catalyst exhibits a high activity, whereas the syngas pretreated sample has a low activity. Moreover, the CO pretreated sample converts during 50 hours of synthesis to a mixture that contains more  $\text{Fe}_3\text{O}_4$  (40%) and less  $\chi\text{-Fe}_{2.2}\text{C}$  (60%) whereas the syngas pretreated sample contains about 80%  $\chi\text{-Fe}_{2.2}\text{C}$  after 50 hours of exposure to synthesis gas. Thus, both catalysts underwent significant changes in the bulk composition without a parallel change in CO conversion. Another catalyst formulation, containing more Cu, much less K, and no binder, showed significantly different activity for syngas conversion following the CO and the syngas activation even though they had a similar bulk phase compositions, with the CO pretreated sample being more active. A catalyst, initially pretreated with syngas and exhibiting low activity, showed evidence for only  $\text{Fe}_3\text{O}_4$ ; this low activity material, following a 24 hour treatment in CO, exhibited a dramatic increase in catalytic activity and the formation of a significant fraction of the carbide phase. The bulk analysis of phase composition is informative about changes in the bulk composition of iron catalysts but these changes do not directly track catalytic activity in many cases.

## INTRODUCTION

Iron catalysts have been used extensively for the Fischer-Tropsch Synthesis (FTS) and are currently the catalysts utilized in the commercial operations at Sasol (1). The iron catalyst permits the production of olefinic products when operated in either the low or high alpha mode (2). The iron catalyst, unlike the cobalt and ruthenium catalysts, forms a carbide under the normal reaction conditions employed in its use. Thus, the composition of the iron catalyst is one aspect that must be elucidated in order to develop a complete understanding of the FTS mechanism (e.g., 3).

In general, pretreatment of an iron catalyst can be accomplished using one of three techniques: CO followed by synthesis gas, H<sub>2</sub> followed by synthesis gas and startup in synthesis gas (e.g., 4-6). Much of the early work was accomplished starting with fused or sintered catalysts and these could only be made active by first reducing to elemental iron in a hydrogen atmosphere (7). Exposure to synthesis gas converted the iron in part or essentially to the carbide. Pretreatment in CO resulted first in the reduction to Fe<sub>3</sub>O<sub>4</sub> and then more slowly to carbides (e.g., 8-10). Pretreating in synthesis gas is more complicated because of the competition between synthesis and carbiding as well as the formation of water that retards the reduction/carbiding steps. Much of the early German work utilized atmospheric or lower pressure start-up pressures when synthesis gas was used (6). It has been claimed that a pretreatment in CO produces an active catalyst that does not require a complex start-up program and is essentially independent of the catalyst composition; however, the start-up procedure used with either synthesis gas or reduction with H<sub>2</sub> followed by synthesis gas appears to depend upon the catalyst formulation (8). In a commercial operation, a synthesis gas

stream is readily available; however, while a pure hydrogen stream may be available it is unlikely that a pure CO stream will be available.

Much of the early characterization of the phases of iron present in FTS catalysts utilized techniques such as X-ray and magnetization; however, these were difficult to make quantitative (7). Mössbauer spectroscopy, because of its sensitivity for iron and its quantitative nature, provides a convenient technique for the characterization of iron FTS catalysts and the changes in composition that they undergo during synthesis. The utilization of a continuous stirred tank reactor (CSTR) permits all of the catalyst charge to be exposed to the same gas composition and, with appropriate experimental technique, to withdraw catalyst samples for characterization at intervals during the pretreatment and synthesis operations. These techniques have been employed in the work that is reported in this communication.

Two of the catalysts utilized in this study were prepared for use in a screening study designed to provide data for the selection of a catalyst for ultimate use in the bubble column reactor at LaPorte, Texas. These two catalysts were prepared by United Catalyst, Inc. according to compositions provided them. The catalyst was formed into spherical particles nominally of about 40-60 micron diameter using a spray drying technique. The third catalyst was formulated at the CAER so that one batch contained copper and the other did not; these batches were prepared for studies to define the role of copper in determining the phases present in the catalyst. At the same time, activity data was obtained so that an attempt could be made to define the role of catalyst phase in determining the catalyst activity.

## EXPERIMENTAL

Three catalyst samples were employed. Two catalysts (UCI 1185-57 containing kaolin and UCI 1185-149-2) were prepared by United Catalysts, Inc. according to specifications set by a consortium in preparation for a run at LaPorte, Texas. The precipitated iron oxide catalyst (prepared at CAER) was prepared by continuous precipitation from aqueous solutions of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and concentrated  $\text{NH}_4\text{OH}$  at pH 10. The precipitate was thoroughly washed with distilled-deionized  $\text{H}_2\text{O}$  and dried at  $120^\circ\text{C}$ .

For a typical test at the CAER, catalyst slurry consisting of 72.7 g of precipitated catalyst and 290 g of  $\text{C}_{30}$  oil (or rather solvents) were mixed inside a 1 L autoclave operated as a continuous stirred tank reactor. The precipitated catalyst slurry was heated to  $270^\circ\text{C}$  at  $1.5 - 2.0^\circ\text{C}/\text{min}$ . under a flow of CO ( $2.0 \text{ nL}/\text{hr-g}(\text{Fe})$ ). CO pretreatment continued at  $270^\circ\text{C}$  for 22 to 24 hours. Following pretreatment, hydrogen flow was started to give a  $\text{H}_2/\text{CO}$  ratio of 0.7 with a flow rate of  $3.4 \text{ nL}/\text{hr-g}(\text{Fe})$ . Catalyst slurry samples were removed ( $\sim 10\text{-}15 \text{ g}$ ) from the reactor at various times of the pretreatment and synthesis. CO and  $\text{H}_2$  conversions were determined by analyzing the exit gas stream with a Carle gas analyzer. Catalyst slurry samples were Soxhlet extracted using refluxing toluene or *o*-xylene to remove accumulated hydrocarbons.

For a typical test conducted at PETC with a CO pretreatment, conditions were slightly different than at CAER. 36.5 g of precipitated catalyst and 370 g of wax were loaded as a 9 wt.% slurry inside a 1 L autoclave. The slurry was heated under a flow of helium at 175 psig to  $150^\circ\text{C}$  and stirred at 1000 rpm. Then heating was continued at  $1^\circ\text{C}/\text{min}$ . under a flow of CO ( $1.4 \text{ nL}/\text{hr-g}(\text{Fe})$ ) to  $270^\circ\text{C}$ . CO pretreatment continued at  $270^\circ\text{C}$  and 175 psig for 22 to 24 hours. Following pretreatment, synthesis gas with a

H<sub>2</sub>/CO ratio of 0.7 was introduced at a rate of 2.4 nL/hr-g(Fe). The synthesis was carried out at 270°C and 175 psig. Catalyst slurry samples (~ 1-3 g) were removed from the reactor. The wax kept the catalyst from oxidizing in air during handling.

For the syngas activation conducted at PETC, the catalyst/wax slurry was heated in flowing helium at 150 psig to 200°C. Then syngas was introduced at 1.8 nL/hr-g(Fe), with an additional 0.6 nL/hr-g(Fe) of helium. The temperature was raised to 280°C and held for 14 hours, again at 150 psig. Following pretreatment, synthesis gas with a H<sub>2</sub>/CO ratio of 0.7 was introduced at a flowrate of 2.4 nL/hr-g(Fe). The pressure was raised to 175 psig and the temperature lowered to 270°C.

The Mössbauer experiments were carried out using a constant acceleration spectrometer. The radioactive source consisted of 50-100 mCi of <sup>57</sup>Co in a Pd matrix. The samples were in powder form and were loaded into Plexiglass compression holders presenting a thin aspect to the gamma ray beam. All spectra were analyzed by a least-squares fitting procedure which models the spectra with a series of Lorentzian peaks. The percentages of the total sample iron contained in each iron-bearing phase identified are determined from the relevant peak areas.

## RESULTS

### 64%Fe<sub>2</sub>O<sub>3</sub>/5%CuO/1%K<sub>2</sub>O/30% Kaolin (UCI-1185-57)

Batches of this catalyst were activated in syngas and in CO. For the CO pretreatment, the catalyst temperature was ramped from 200 to 270°C at 1.5°C/min under CO at 13 atm; it was maintained at 270°C in a CO flow of 2.0 NL/hr.-gFe during the remainder of a 24 hour period. During this pretreatment the iron oxide in the catalyst was first reduced to Fe<sub>3</sub>O<sub>4</sub> and then converted to iron carbide. At the end of the 24 hour pretreatment, the catalyst contained about 90% χ-Fe<sub>5</sub>C<sub>2</sub> with the remainder

of the iron being present in a superparamagnetic form (figure 1). Low temperature (12 K) Mössbauer measurements on one of the samples of withdrawn catalyst showed that the superparamagnetic (spm) phase was  $\text{Fe}_3\text{O}_4$ , and not the carbide which can also be present in a spm phase. During synthesis the amount of  $\chi\text{-Fe}_5\text{C}_2$  decreased to about 60% during 30 hours and remained at about this level (figure 1). The CO pretreated catalyst exhibited a conversion ( $\text{H}_2 + \text{CO}$ ) in the 70-80% range during 150 hours of synthesis (figure 2).

A portion of the catalyst was pretreated in synthesis gas. This was accomplished by heating the slurry to  $200^\circ\text{C}$  in He and then switching to synthesis gas ( $\text{H}_2/\text{CO} = 0.67$ ) at  $150^\circ\text{C}$  after which the sample was heated to  $280^\circ\text{C}$  at a rate of  $7.0^\circ\text{C}/\text{min}$ . After holding the catalyst at  $280^\circ\text{C}$  in a flow of synthesis gas for 12 hours, the pressure was increased to 20 atm and the temperature was lowered to  $265^\circ\text{C}$ . These conditions for the pretreatment (activation) and synthesis were chosen to correspond to the conditions used for Run 2 at the LaPorte, Texas slurry bubble reactor demonstration plant. The catalyst was rapidly converted to magnetite and then the magnetite was slowly converted to iron carbides. At the end of the pretreatment (activation) period, about 40% of the iron was present as a mixture of  $\chi\text{-Fe}_5\text{C}_2$  and  $\epsilon\text{-Fe}_{2.2}\text{C}$  (figure 3). During 24 hours of synthesis, the catalyst composition changed so that it contained almost 80%  $\chi\text{-Fe}_5\text{C}_2$  and  $\epsilon\text{-Fe}_{2.2}\text{C}$ .

As can be seen in figure 2, the conversion of syngas was increasing during the pretreatment period, and had attained about 60%. During this period the amount of carbide was increasing and attained a level of about 40%. Almost immediately after the change of conditions to those used for the synthesis, the conversion dropped to the 20-30% level. At this low conversion level the formation of carbide continued to exceed

that of the CO pretreated catalyst at an equivalent time on stream. The different levels of carbide present during the synthesis is considered to be controlled primarily by the level of conversion of the syngas, and not by the different pretreatments. A high level of (H<sub>2</sub> + CO) conversion produces CO<sub>2</sub> and H<sub>2</sub>O, which are oxidizing gases. On the other hand, for low (H<sub>2</sub> + CO) conversions, the catalyst is exposed to a reducing atmosphere.

#### 57.2%Fe/9.3%Cu/0.05%K

This catalyst differs from the one described above since it does not contain the Kaolin binder (support), contains almost twice as much copper and only about one-twentieth as much potassium. The catalyst was pretreated in CO under the conditions normally employed at the CAER (1.4 NL/hr.-gFe of CO at 13 atm, 270°C, 22 hr). The composition of the catalyst underwent a decrease in the amount of superparamagnetic magnetite present as well as a decrease in the amount of magnetically ordered magnetite. During synthesis the amount of  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> increased from the 30-40% level to about 70% (Table 1). At the same time there was a decrease in the amount of superparamagnetic magnetite, and then the Fe<sub>3</sub>O<sub>4</sub>; apparently the superparamagnetic material is converted to the carbide more rapidly than the magnetically ordered Fe<sub>3</sub>O<sub>4</sub> is. During synthesis time, the conversion dropped from about 90% to the 50% level. This drop is typical with this type of heavy wax used as startup solvent, as discussed below.

The catalyst pretreated in synthesis gas had a poor activity, with the conversion in the 5-20% range (Table 2). At the end of the 14 hour activation period the catalyst contained 36%  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>. After 26 hours of synthesis the amount of  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> had

increased to 84% and this increased to 91% after 49 hours. This test was conducted in a light wax,  $n$ -octacosane.

Pretreatment of this catalyst in CO was conducted in two solvents: for comparison, purified  $n$ -octacosane and the residue of a vacuum distillation of an Allied-Signal wax (comprised of predominantly  $C_{40+}$ ) were used. Similar results were obtained in both solvents. In the  $C_{28}$  wax, the catalyst contained 86%  $\chi$ - $Fe_5C_2$  following the 22 hour pretreatment in CO and this phase declined to about 55% during 160 hours of synthesis (Table 3). During the synthesis the  $\chi$ - $Fe_5C_2$  appears to be converted predominately to the superparamagnetic material rather than magnetically ordered  $Fe_3O_4$ . It appears that the fraction of iron present in the  $\chi$ - $Fe_5C_2$  phase was slightly lower in the heavy solvent than in the lower molecular weight wax (64 versus 86%) (Tables 3 and 4). During the synthesis the carbide phase decreases with a corresponding increase in the superparamagnetic material. In both solvents a small fraction (0.06-0.12) of  $\epsilon$ - $Fe_{2.2}C$  is formed during the initial period of the CO pretreatment, but this phase is not observed following about 10 hours of pretreatment.

The activity of the catalyst is similar in the two solvents during the first 100 hours; however, the conversion is slightly lower in the higher boiling wax and declines more quickly after 100 hours on stream.

#### 100 Fe/3.6 Si/0.71 K

This catalyst was initially pretreated in synthesis gas and then used for synthesis. Following a period of synthesis the catalyst was subjected to a pretreatment in CO, and this was followed by a period of synthesis. The CO pretreatment caused a dramatic increase in the synthesis gas conversion; details of this as well as the impact of pressure of the synthesis gas used during pretreatment on the activity are reported in



detail elsewhere (11). The catalyst was exposed to synthesis gas ( $H_2/CO = 0.67$ ) at  $270^\circ C$ , 13 atm., and a flow of 3.1 NL/hr.-gFe. After six hours the catalyst contained 25% magnetically ordered  $Fe_3O_4$  and 75% superparamagnetic phase (Table 5). During the next 87 hours, the amount of the superparamagnetic phase decreased below the detectable limit, and the sample was essentially 100% magnetically ordered  $Fe_3O_4$ . During this period the synthesis gas conversion was in the range of 9-12%. A surface layer (or partial layer) of  $\chi$ - $Fe_5C_2$  or spm  $\chi$ - $Fe_5C_2$  may be present, but undetected by the Mössbauer measurements, and this was responsible for the small syngas conversion that was observed.

Following the 93 hours exposure to synthesis gas, the hydrogen flow was stopped so that the sample was exposed to only CO at  $270^\circ$  and 13 atm. during a 22 hour period. At the end of this 22 hour period the catalyst contained 58% magnetically ordered  $Fe_3O_4$ , 9% of the superparamagnetic phase and 33%  $\chi$ - $Fe_5C_2$ . Shortly after hydrogen was reintroduced so that the catalyst was again exposed to the synthesis gas, the conversion increased to 25% and within 4 hours (119.5 hours total) had attained a conversion level of 59%. Within 77 hours following the CO only treatment, the syngas conversion was 88% and remained at or above 80% during the 500 hours of the test. There was little change in the composition of the catalyst following the treatment with CO. Thus, the CO treatment caused the conversion of about one-third of the iron to the carbide form and this resulted in an increase in the conversion to greater than 80%. It is therefore apparent that the nearly 100 hour exposure to synthesis gas did not impact the catalyst so as to inhibit the subsequent activation by CO. Furthermore, the subsequent CO pretreatment produced a catalytic material that had an activity that was essentially the same as if the catalyst had been pretreated initially with CO. Other runs

with different portions of this catalyst batch show that the conversion level will remain low even if synthesis gas flow had been continued for hundreds of hours without the CO pretreatment; furthermore, the amount of carbide would slowly increase at longer times on stream.

Another portion of the catalyst was pretreated in syngas under identical conditions as used above except that the total pressure was held at 1 atm for a 24 hour period before increasing to the synthesis conditions (13 atm, 270°C, 3.1 NL/hr.-gFe,  $H_2/CO = 0.67$ ), and the results are given in Table 6. After the 24 hour period at atmospheric pressure, the catalyst was composed of 41%  $\chi$ - $Fe_5C_2$ , 27% superparamagnetic phase and 32% magnetically ordered  $Fe_3O_4$ . After 24 hours at 13 atm pressure, the conversion was 82%. The conversion declined slowly to 69% during the 384 hour run. It is therefore apparent that the low pressure treatment with synthesis gas led to the formation of a significant quantity of carbide whereas this was not the case when the treatment was carried out at 13 atm. In addition, the presence of iron carbide lead to a catalyst with high activity whereas the catalyst that did not contain a detectable amount of carbide had low activity.

As a means of evaluating the role of copper upon the activation, the 100Fe/3.6Si/0.71K catalyst was impregnated with sufficient aqueous copper nitrate to give 2.6 atomic % Cu relative to Fe. This catalyst was then utilized for the synthesis (13 atm,  $H_2/CO = 0.67$ , 270°C and 3.1 NL/hr-gFe) without prior activation. After 4.3 hours, the sample consisted of 19% superparamagnetic phase (carbide and/or oxide) and 81% magnetically ordered  $Fe_3O_4$  (table 7). Continuing the reaction resulted in a decrease in the superparamagnetic phase with an increase in the magnetically ordered  $Fe_3O_4$ . At 114 hours of synthesis the superparamagnetic phase corresponded to only

3% and there was 15%  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>; the carbide phase increased to 20% after 215 hours on stream. The conversion of synthesis gas was higher when copper was present than when it was absent; this is true whether a carbide phase is present or not. Thus after 19 hours in syngas the Cu containing material produced 26% conversion whereas the same catalyst without Cu produced only about 10% conversion. The conversion continued to increase with time on stream when Cu was present but this did not appear to be the case when Cu was not present. After 215 hours on stream, the activity of the Cu-containing catalyst had increased to provide about 50% syngas conversion.

## DISCUSSION

For the Kaolin containing catalyst only the  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> carbide phase was observed. However, when the same catalyst was pretreated with synthesis gas, both  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and  $\epsilon$ -Fe<sub>2.2</sub>C were observed; however, these carbides are observed when the conversion was low. Furthermore, the CO pretreatment leads to a high fraction of the carbide phase and to high catalytic activity. With increasing time on stream the amount of the carbide phase decreases while the conversion remains essentially constant. Thus, the catalyst undergoes changes in chemical composition while the catalyst activity and selectivity (11) both remain essentially constant. On the other hand, treating the catalyst in synthesis gas at 13 atm leads to a material which produces low synthesis gas conversion. Under these low conversion conditions, the fraction of iron present as a carbide phase gradually increases to exceed that of the CO pretreated sample.

An iron catalyst containing much less potassium (0.05%) and no support produced a significant amount of carbide for both the CO and syngas pretreatment. However, the activity of the catalyst pretreated with CO was significantly greater than the one pretreated in syngas. The activities for the material pretreated by the two ways

were quite different when the catalysts contained the same amount of carbide. Thus, when about 40% of the iron was present as a carbide, the CO pretreated sample provided 84% syngas conversion (at 84 hours on stream) whereas the syngas sample produced a conversion that was very low (<5% at 14 hours on stream). As the carbide fraction of the CO pretreated sample increased with time on stream the synthesis gas conversion decreased. Thus, it is necessary for some carbide to be present to have a catalyst with a high activity; however, it is evident that the activity of the material cannot be predicted solely from the fraction of iron that is present as the carbide.

In general, the CO pretreated samples have a high activity and a high fraction of the iron present as the carbide phase; with increasing time on stream the fraction of iron carbide decreases. The fraction of iron present as the carbide following the CO pretreatment appears to depend upon the composition of the catalyst. However, if the relative fraction of iron carbide that is converted to the oxide with time on stream is considered; the iron carbide fraction of each catalyst was converted to the oxide at about the same rate with time on stream (figure 4). There is a rapid conversion of the carbide to the oxide as the sample is initially exposed to the synthesis gas; however, after about 40 hours the fraction of carbide remaining (about 0.6 of the initial amount) attains a pseudo steady state. It must be kept in mind that the general scheme illustrated in figure 4 applies only to those catalysts that have a high activity, and is not intended to apply to all possible experimental conditions. The data in figure 4 include a catalyst that has been pretreated with synthesis gas at 1 atm; therefore, the low pressure activation in synthesis gas appears to resemble an activation in CO.

In general, when a catalyst activation produces both an active catalyst and a high fraction of iron carbide, there will be a conversion of the carbide to the oxide and

the attainment of a pseudo steady state composition. A material whose pretreatment produces a catalyst with a low activity and a low fraction of iron carbide will undergo carbiding with time on stream to approach nearly complete carbide formation. Much of the characterization data in the literature has been generated using experimental conditions that correspond to low conversion conditions (reducing atmosphere). Consequently, the fact that these materials exhibit complete, or nearly complete, carbide phase is considered to be more dependent upon the low conversion conditions than upon the catalyst.

In summary, it appears that the presence of some fraction of iron carbide is necessary for a material to exhibit a high (>80%) conversion; however, the presence of carbide is not a sufficient condition for high activity. Furthermore, the current data is in agreement with the observation that the catalytic activity and selectivity will remain essentially constant while the catalyst undergoes significant chemical and/or phase changes. It is therefore not possible to predict the catalyst performance based upon the bulk analysis of the catalyst. However, when the bulk analysis of the catalyst, at the end of the activation step shows no carbide present, the catalyst performance can be predicted to be poor.

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Table 1

Catalyst: UCI 1185-149-2 (57.2 Fe/9.3 Cu/0.05 K)  
 Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe)  
 FT Synthesis Conditions: H<sub>2</sub>/CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)  
 9% Catalyst Loading in Distilled Allied-Signal Heavy Wax of 370 g

Sample	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	SPM	(H <sub>2</sub> + CO), Conversion %*
FT Run TOS = 84 hrs	40	37	23	84.0
FT Run TOS = 235 hrs	60	30	10	67.7
FT Run TOS = 305 hrs	68	27	5	51.2

\* FT synthesis runs were carried out at PETC.

Table 2

Catalyst: UCI 1185-149-2 (57.2 Fe/9.3 Cu/0.05 K)  
 Activated in H<sub>2</sub>/CO/HE at 270°C, 175 psig, 22 hr, 1.8 nL syngas/hr-g(Fe)  
 FT Synthesis Conditions: H<sub>2</sub>/CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)  
 9% Catalyst Loading in C-28 Light Wax of 370 g

Sample	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	SPM Phase	(H <sub>2</sub> + CO), Conversion %*
Activated for 14 hrs	36	48	16	---
FT Run TOS = 26 hrs	84	14	2	16
FT Run TOS = 49 hrs	91	7	2	6

\* FT synthesis runs were carried out at PETC.



Table 3

## FT Synthesis in Light Wax

Catalyst: UCI 1185-149-3 (57.2 Fe/9.3 Cu/0.05 K)  
 Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe)  
 Synthesis Conditions: H<sub>2</sub>/CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)  
 9% Catalyst Loading in C28, n-octacosane, Light Wax of 370 g

Sample	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	SPM Phase	$\epsilon$ -Fe <sub>22,2</sub> C	(H <sub>2</sub> + CO), Conversion %
Activated for 2 hrs	---	82	6	12	---
Activated for 18 hrs	77	21	2	---	---
Activated for 22 hrs	86	12	2	---	---
FT Run TOS = 19.5 hrs	58	15	27	---	89
FT Run TOS = 43 hrs	56	16	28	---	91
FT Run TOS = 90 hrs	65	20	15	---	91
FT Run TOS = 160 hrs	56	21	23	---	91

Table 4

## FT Synthesis in Heavy Wax

Catalyst: UCI 1185-149-3 (57.2 Fe/9.3 Cu/0.05 K)  
 Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe)  
 Synthesis Conditions: H<sub>2</sub>/CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)  
 9% Catalyst Loading in Distilled Allied-Signal Wax of 370 g

Sample	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	SPM Phase	$\epsilon$ -Fe <sub>22,2</sub> C	(H <sub>2</sub> + CO), Conversion %*
Activated for 2 hrs	---	88	6	6	---
Activated for 9.5 hrs	54	37	9	---	---
Activated for 22 hrs	64	27	9	---	---
FT Run TOS = 24 hrs	42	30	28	---	81
FT Run TOS = 47.5 hrs	39	34	27	---	87
FT Run TOS = 94.5 hrs	37	40	23	---	86

\*The SPM phase is likely to be  $\alpha$ -FeOOH as revealed by low temperature measurements on UCI 1185-149-3 catalyst subjected to CO activation and 24 hrs of FT synthesis.

Table 5

Activation Carried out at High Pressure (12 atm)

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

Initial Activation in Syngas at 12 atm, 270°C, H<sub>2</sub>/CO = 0.7, S.V. = 3.4 nL/hr-g(Fe)Synthesis Conditions: 270°C, 175 psig, 3.4 nL/hr-g(Fe), H<sub>2</sub>/CO = 0.7

Catalyst	SPM Phase	Fe <sub>3</sub> O <sub>4</sub>	χ-Fe <sub>5</sub> C <sub>2</sub>	Conversion %
Syngas: TOS = 6.33 hrs	75	25	---	9.2
Syngas: TOS = 24.0 hrs	31	69	---	9.7
Syngas: TOS = 46.0 hrs	11	89	---	11.5
Syngas: TOS = 93.0 hrs	---	100	---	12.2
CO: TOS = 115 hrs	9	58	33	
Syngas: TOS = 119.5 hrs	15	60	25	59
Syngas: TOS = 192.5 hrs	18	63	19	88
Syngas: TOS = 313 hrs	13	67	20	86
Syngas: TOS = 456.0 hrs	11	63	26	81

Table 6

Pretreatment Carried out at Low Pressure (1 atm)

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

Activation Conditions: 270°C, 1 atm, H<sub>2</sub>/CO = 0.7, S.V. = 3.4 nL/hr-g(Fe), 24 hrsSynthesis Conditions: 270°C, 13 atm, S.V. = 3.4 nL/hr-g(Fe), H<sub>2</sub>/CO = 0.7

Sample	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	SPM Phase	(H <sub>2</sub> + CO) Conversion %
Activated for 24 hrs	41	32	27	---
FT Run TOS = 24 hrs	36	40	24	82.0
FT Run TOS = 48 hrs	31	47	22	83.0
FT Run TOS = 95 hrs	33	48	19	79
FT Run TOS = 218 hrs	26	50	24	75
FT Run TOS = 384 hrs	20	60	20	69

Table 7

Pretreatment Carried out at High Pressure (12 atm)

Catalyst: 100 Fe/3.6 Si/2.6 Cu/0.71 K (atomic % relative to Fe)

Initial Activation in Syngas at 12 atm, 270°C, H<sub>2</sub>/CO = 0.7, S.V. = 3.4 nL/hr-g(Fe)

Synthesis Conditions: 270°C, 175 psig, 3.4 nL/hr-g(Fe), H<sub>2</sub>/CO = 0.7

Catalyst	SPM Phase	Fe <sub>3</sub> O <sub>4</sub>	χ-Fe <sub>5</sub> C <sub>2</sub>	Conversion %
TOS = 4.33 hrs	19	81	---	26
TOS = 21.0 hrs	10	90	---	26
TOS = 45.0 hrs	14	86	---	32
TOS = 113.7 hrs	3	82	15	43
TOS = 214.5 hrs	4	76	20	51

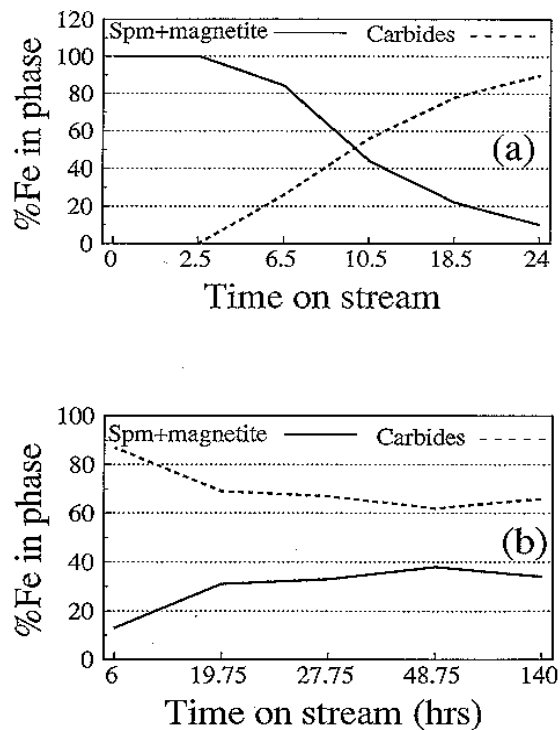


Figure 1. Iron phase distribution in the catalyst UCI 1185-57 versus TOS (a) during activation in CO, and (b) during FT synthesis.

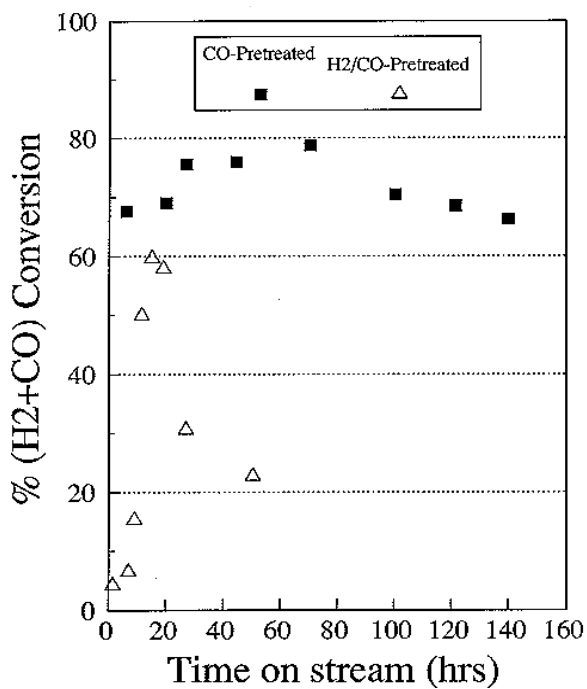


Figure 2. (H<sub>2</sub> + CO) conversion dependence on pretreatment.

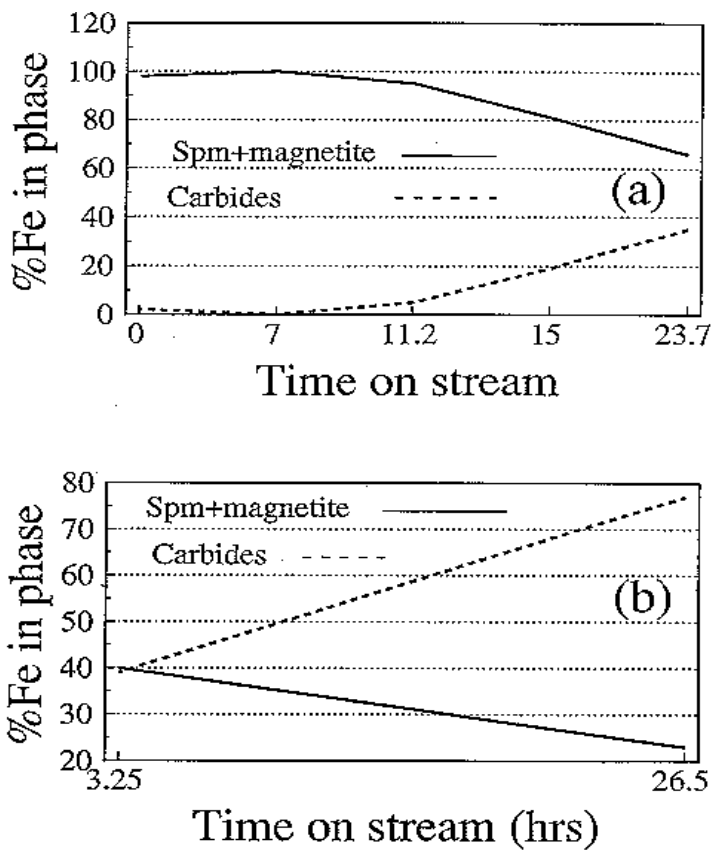


Figure 3. Iron phase distribution in the catalyst UCI 1185-57 versus TOS (a) during activation in syngas, and (b) during FT synthesis.

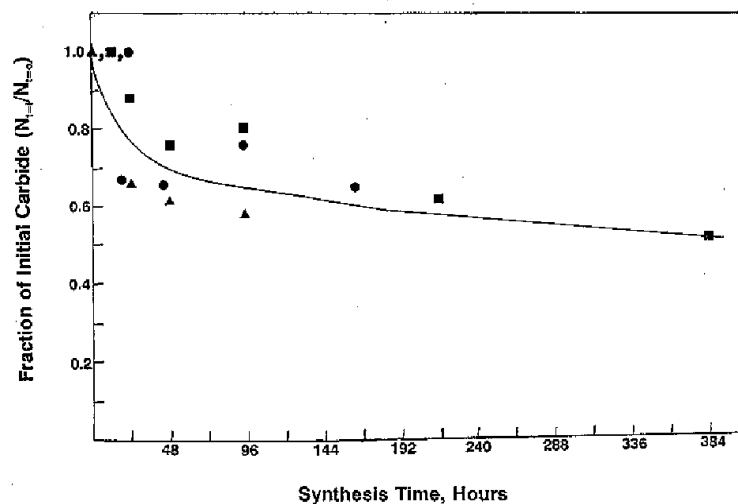


Figure 4. The fraction of the initial carbide remaining after increasing time on stream (▲, UCI 1185-149 (syngas, Table 4); ●, UCI 1185-149 (CO, Table 3); ■, 100 Fe/3.6 Si/0.71 K (syngas, 1 atm, Table 6).