

**VI.8. FISCHER-TROPSCH SYNTHESIS AND XRD CHARACTERIZATION OF AN IRON CARBIDE CATALYST SYNTHESIZED BY LASER PYROLYSIS (Robert J. O'Brien, Liguang Xu, Xiangxin Bi, Peter Eklund and Burtron H. Davis).**

**VI.8.1. ABSTRACT**

Iron carbide catalysts prepared by laser pyrolysis and from carbiding a commercially ultrafine iron oxide (or oxyhydroxide) are not as active for FTS as one prepared by carbiding one obtained using a precipitation procedure. However, for the same CO conversion, the catalyst prepared by laser pyrolysis was more selective for hydrocarbon production, mainly because of a lower water-gas-shift activity. During the course of synthesis all three catalysts were gradually oxidized to convert the iron carbide to predominantly an iron oxide.

**VI.8.2. INTRODUCTION**

Carbides have been implicated as possible reactive species for iron based Fischer-Tropsch catalysts (VI.8.1-VI.8.3). Iron carbides which have been identified during the Fischer-Tropsch Synthesis (FTS) include:  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>,  $\epsilon'$ -Fe<sub>2.2</sub>C,  $\theta$ -Fe<sub>3</sub>C and Fe<sub>7</sub>C<sub>3</sub> (VI.8.4-VI.8.7). Reducing catalysts to  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and  $\epsilon'$ -Fe<sub>2.2</sub>C with CO has proven to be an effective procedure for activating iron based Fischer-Tropsch catalysts. Limited studies have also shown that iron carbides synthesized by the laser pyrolysis of iron carbonyl and ethylene are active for the FTS (VI.8.8-VI.8.10). Rice et al. have reported that a near stoichiometric  $\theta$ -Fe<sub>3</sub>C catalyst, produced by laser pyrolysis and operating at 270°C, 75 psig and H<sub>2</sub>/CO=2 had a higher selectivity for olefins and C<sub>5</sub>+ hydrocarbons than a spinel Fe-Co catalyst; however, the iron carbide catalyst was not as active as the Fe-Co catalyst and the data were compared at

different conversions (VI.8.8). Soled et al. reported that the olefin selectivity of a  $\theta$ - $\text{Fe}_3\text{C}$  catalyst synthesized by laser pyrolysis is not effected by potassium promotion as are precipitated iron oxide catalysts (VI.8.10). It was concluded that the precipitated catalysts contain acidic sites on the surface of the catalysts which promote secondary reactions. Herein are reported the catalyst characterization and slurry phase Fischer-Tropsch activity studies of an iron carbide catalyst prepared by laser pyrolysis. A comparison is made to an unpromoted precipitated iron catalyst pretreated with CO.

### VI.8.3. EXPERIMENTAL

An iron oxide catalyst and an iron carbide catalyst were used. The iron oxide catalyst 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  $120^\circ\text{C}$ . The iron carbide catalyst was prepared by pyrolysis of  $\text{Fe}(\text{CO})_5$  and  $\text{C}_2\text{H}_4$  with a  $\text{CO}_2$  laser using a similar procedure to that reported by Rice et al. (VI.8.8). The batch of catalyst used in this study was collected in a  $\text{C}_{30}$  oil (Ethylflo) during its synthesis in order to minimize oxidation of the catalyst during transfer to the Fischer-Tropsch reactor; therefore, this batch was not characterized prior to the FTS experiment. Previously produced batches of catalyst prepared using this procedure were determined to be comprised of  $\theta$ - $\text{Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  with particle sizes  $<300 \text{ \AA}$  and surface areas of  $\sim 70 \text{ m}^2/\text{g}$ .

Catalyst slurries consisting of 72.7 g of precipitated catalyst or 12.0 g of iron carbide and 290 g of  $\text{C}_{30}$  oil were mixed inside a 1 L autoclave operated as a continuous stirred tank reactor (Figure VI.8.1). The precipitated catalyst slurry was heated to  $270^\circ\text{C}$  at  $1.5\text{-}2.0^\circ\text{C}/\text{min}$  under a flow of CO ( $2.0 \text{ nL}/\text{hr-g}(\text{Fe})$ ). CO

pretreatment continued at 270°C for 24 hr. Following pretreatment, hydrogen flow was started to give a H<sub>2</sub>/CO ratio of 0.7 with a flow rate of 3.4 nL/hr-g(Fe). The iron carbide catalyst slurry was heated to 270°C under CO at 2.0 nL/hr-g(Fe) synthesis gas (H<sub>2</sub>/CO=0.7) was then started at a flow rate of 3.4 nL/hr-g-Fe. Catalyst slurry samples were removed (~ 10-15 g) from the reactor at various times of the pretreatment and synthesis. CO and H<sub>2</sub> 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.

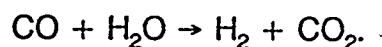
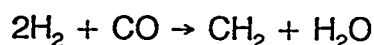
Powder X-ray diffraction patterns of the catalysts were obtained using a Philips APD X-ray diffraction spectrometer equipped with a Cu anode and Ni filter operated at 40 kV and 20 mA (CuK $\alpha$ =1.5418 Å). Iron phases were identified by comparing diffraction patterns of the catalyst samples with those in the standard powder X-ray diffraction file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data.

#### VI.8.4. RESULTS AND DISCUSSION

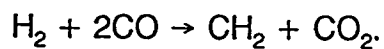
Conversion data as a function of time of synthesis for the two catalysts are shown in Figures VI.8.2 and VI.8.3. In general the precipitated catalyst is more active than the iron carbide catalyst with syn-gas conversions starting at 80% as compared to 50% for the latter; however, both catalysts deactivated with increasing reaction time. A comparison of the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> olefin selectivities at 26% CO conversion (precipitated catalyst-336 hr of synthesis, iron carbide catalyst-122 hr of synthesis) are shown in Figure VI.8.4. Surprisingly the precipitated catalyst had a higher olefin content than the iron carbide catalyst. It has been reported that a similar iron carbide

catalyst has higher selectivity for the production of olefins than a "conventionally prepared" Fe/Co catalyst (VI.8.8). The discrepancy may be due in part to comparing the olefin selectivity of the two catalysts at different conversions. Their "conventional catalyst" had a C<sub>2</sub>-C<sub>4</sub> olefin content of 37% at 72% conversion compared to 86% olefin at 55% conversion for the iron carbide catalyst (VI.8.8). In general the olefin selectivity of a catalyst is highest at low conversions. The iron carbide catalyst of this study produces more hydrocarbons than the precipitated catalyst; furthermore, it produces a higher fraction of C<sub>3</sub>+ (86% vs. 84%) and C<sub>5</sub>+ (67% vs. 61%) hydrocarbons (Figure VI.8.5). Correspondingly, the iron carbide catalyst produces less methane and ethane than the precipitated catalyst (Figure VI.8.6). These hydrocarbon and C<sub>5</sub>+ selectivities are similar to those reported earlier (VI.8.8-VI.8.10).

The relevant reactions for the iron catalyzed Fischer-Tropsch synthesis are:



When the water-gas shift is high, the overall reaction can be written as



The ratio of CO<sub>2</sub> produced to CO converted is 0.5 for this case. The CO<sub>2</sub>/CO ratio is 0.33 for the precipitated catalyst and 0.24 for the iron carbide catalyst at 26% CO conversion. This is a good indication that the precipitated catalyst has a higher water-gas shift activity than the iron carbide catalyst. The higher water-gas shift activity would account for the lower hydrocarbon production of the precipitated catalyst since more CO is being converted to CO<sub>2</sub>.

#### VI.8.4.a. Characterization

Heating the precipitated catalyst from 25°C to 270°C (2 hr) under CO rapidly reduced the catalyst to  $\text{Fe}_3\text{O}_4$  (Figure VI.8.7). Further reduction to iron carbides during the CO pretreatment proceeded much more slowly. After 3.5 hr of CO pretreatment at 270°C, XRD showed trace amounts of  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  and  $\chi$ - $\text{Fe}_5\text{C}_2$ . After 10 hr at 270°C, the carbide phases were more distinct; however,  $\text{Fe}_3\text{O}_4$  was still the dominant phase. After the completion of the pretreatment, 24 hr at 270°C, the catalyst consisted of a mixture of  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  and  $\chi$ - $\text{Fe}_5\text{C}_2$  with a substantial amount of  $\text{Fe}_3\text{O}_4$ . During the first 2 hr of exposure to synthesis conditions the peaks associated with the  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  and  $\chi$ - $\text{Fe}_5\text{C}_2$  phases increased in intensity; however, during the remainder of the run, the carbide phases decreased as the intensity of the peaks associated with  $\text{Fe}_3\text{O}_4$  increased. After 336 hr of synthesis the catalyst had essentially reoxidized to  $\text{Fe}_3\text{O}_4$ .

Similar results were obtained for the iron carbide catalyst (Figure VI.8.8). XRD of the catalyst following heat-up to 270°C in CO showed predominantly  $\theta$ - $\text{Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  with a small amount of  $\text{Fe}_3\text{O}_4$ . The  $\text{Fe}_3\text{O}_4$  peaks grew in intensity during the first 25 hr of synthesis and after 50 hr of synthesis,  $\text{Fe}_3\text{O}_4$  was the dominant phase. The XRD of the catalyst after 190 hr of synthesis showed only  $\text{Fe}_3\text{O}_4$ .

The oxidation of iron carbides during the Fischer-Tropsch synthesis has been well established (VI.8.4, VI.8.11-VI.8.13). Synthesis gas is reducing; however, as the concentrations of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  increase due to the Fischer-Tropsch and water-gas shift reactions the gas in the reactor becomes oxidizing. A  $\text{H}_2\text{O}/\text{H}_2$  ratio of  $\sim 0.02$  and a  $\text{CO}_2/\text{CO}$  ratio of  $\sim 2$  are necessary for  $\text{Fe}_3\text{O}_4$  to be thermodynamically stable at the

synthesis conditions used in this study (VI.8.14). The concentration of  $\text{CO}_2$  was not high enough to be oxidizing for the iron carbide catalyst; however, the  $\text{H}_2\text{O}/\text{H}_2$  ratio (0.08-0.2) was high enough to oxidize the catalyst to  $\text{Fe}_3\text{O}_4$ . Likewise the  $\text{H}_2\text{O}$  concentration was sufficient to oxidize the precipitated catalyst ( $\text{H}_2\text{O}/\text{H}_2=0.2$ ) as was the  $\text{CO}_2$  concentration at the beginning of the run ( $\text{CO}_2/\text{CO}=2.5$ ).

The typical BET surface area of the freshly prepared iron carbide catalyst is approximately  $70 \text{ m}^2/\text{g}$ . The surface area of the precipitated catalyst before pretreatment was  $140 \text{ m}^2/\text{g}$ ; however, following pretreatment with CO at  $270^\circ\text{C}$  the surface area dropped to  $32 \text{ m}^2/\text{g}$ . The particle sizes of the catalysts after 170 hr, determined by X-ray line broadening, are  $270 \text{ \AA}$  and  $300 \text{ \AA}$  for the iron carbide and precipitated catalysts respectively. A particle size in this range corresponds to a surface area of about  $40 \text{ m}^2/\text{g}$  which implies that the difference in activity is not due to a difference in surface area.

#### VI.8.5. CONCLUSIONS

In general it was found that an iron carbide catalyst prepared by laser pyrolysis is not as active as a precipitated iron catalyst pretreated with CO. However, at similar low CO conversion, the iron carbide catalyst produces more hydrocarbons and has a higher selectivity for  $\text{C}_5+$  hydrocarbons. The hydrocarbon yield is impacted by the extent of the water-gas-shift. Differences in activity and selectivity may be due to the iron carbide phases present on the catalyst surface. The catalyst prepared by laser pyrolysis appeared by XRD to be mostly a mixture of  $\theta\text{-Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  at the start of the synthesis; whereas, the CO pretreated catalyst contained the carbides  $\chi\text{-Fe}_5\text{C}_2$  and  $\epsilon'\text{-Fe}_{22}\text{C}$ . Exposure to synthesis conditions brought about the oxidation of both

catalysts to essentially 100% bulk  $\text{Fe}_3\text{O}_4$ ; however, this does not rule out the possibility that the carbides survived on the surface of the catalyst.

## VI.8.6. REFERENCES

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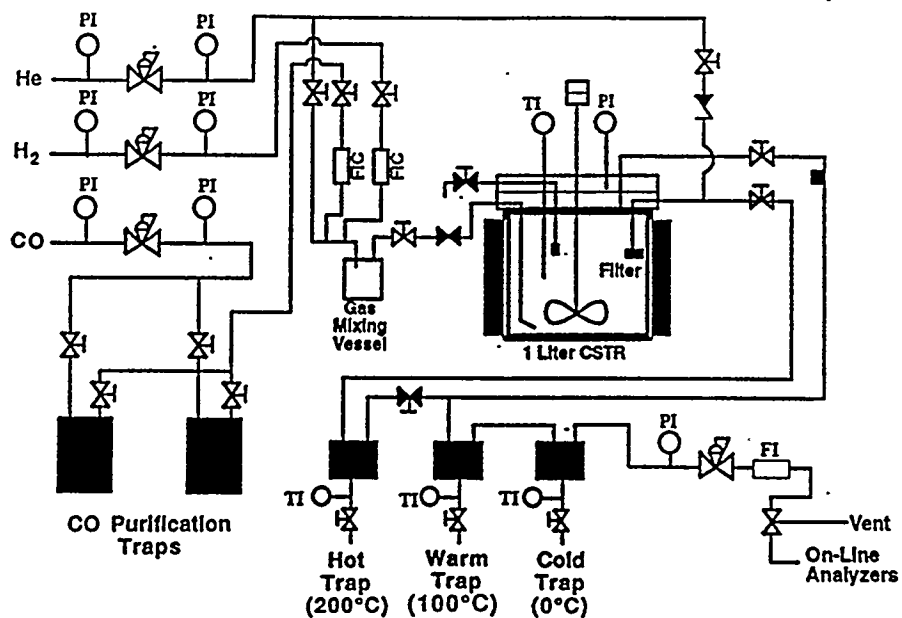


Figure VI.8.1. Reactor configuration for 1 L CSTR.

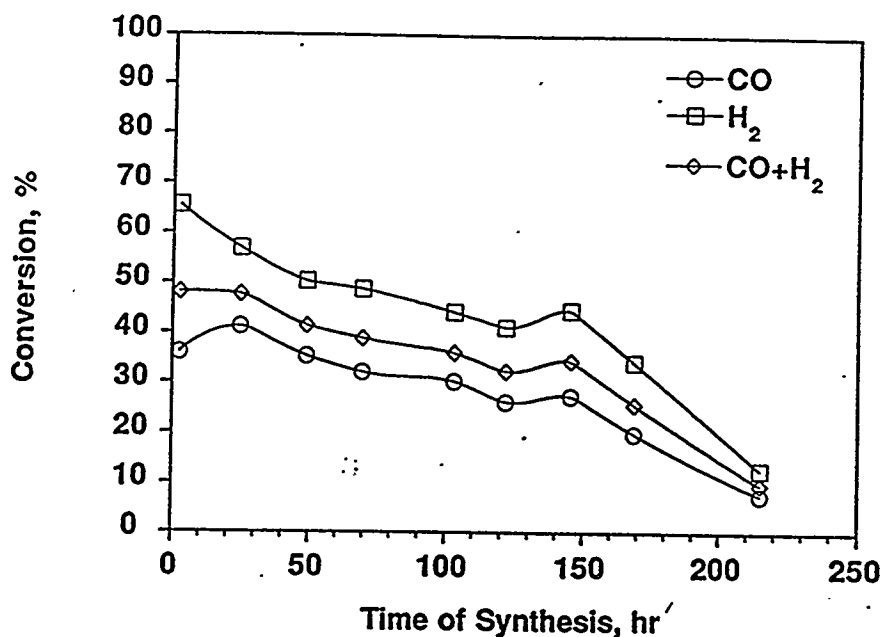


Figure VI.8.2. Synthesis gas conversion data as a function of time of synthesis for the iron carbide catalyst synthesized by laser pyrolysis.

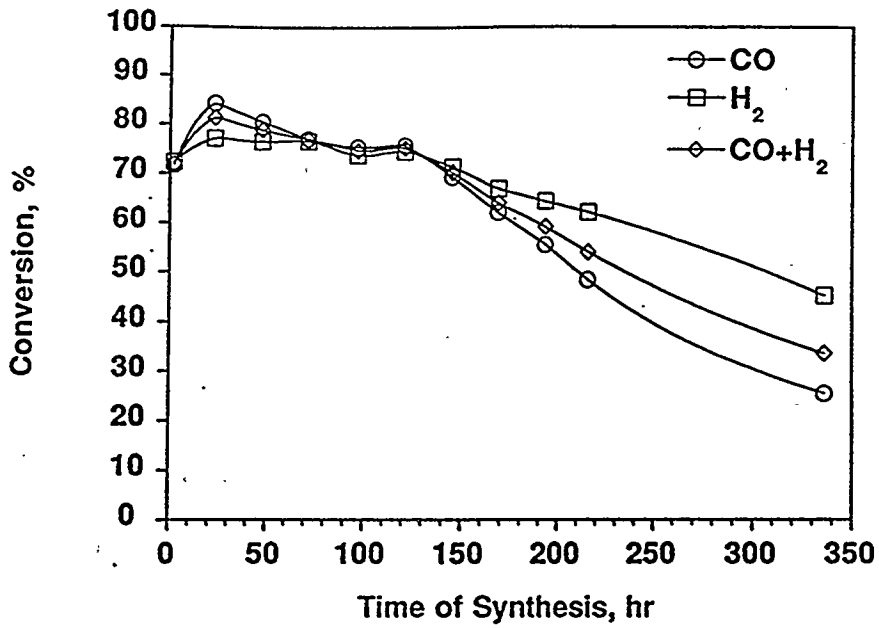


Figure VI.8.3. Synthesis gas conversion data as a function of time of synthesis for the precipitated iron oxide catalyst pretreated with CO.

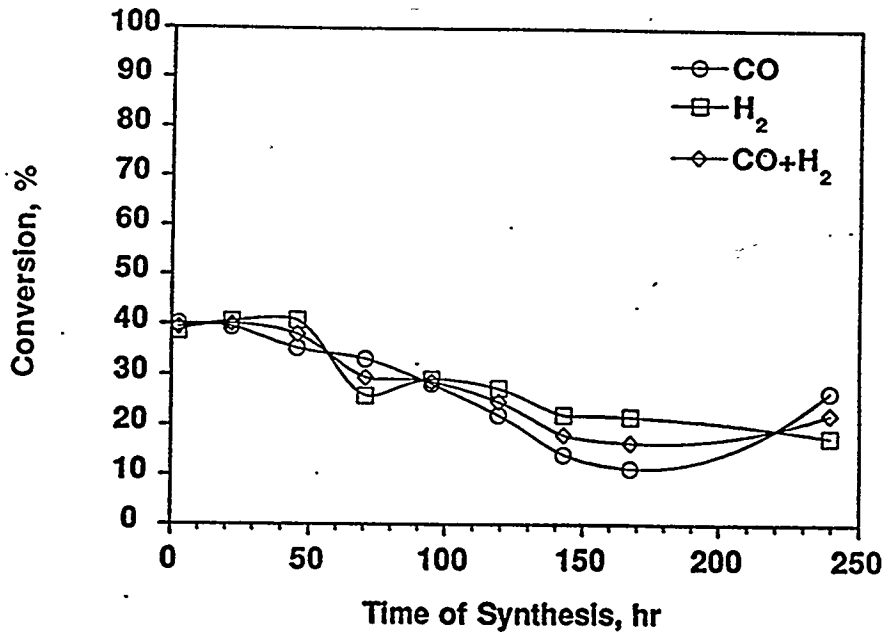


Figure VI.8.4. Comparison of the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> olefin fraction at 26% CO conversion for the iron carbide catalyst and the precipitated iron oxide catalyst pretreated with CO.

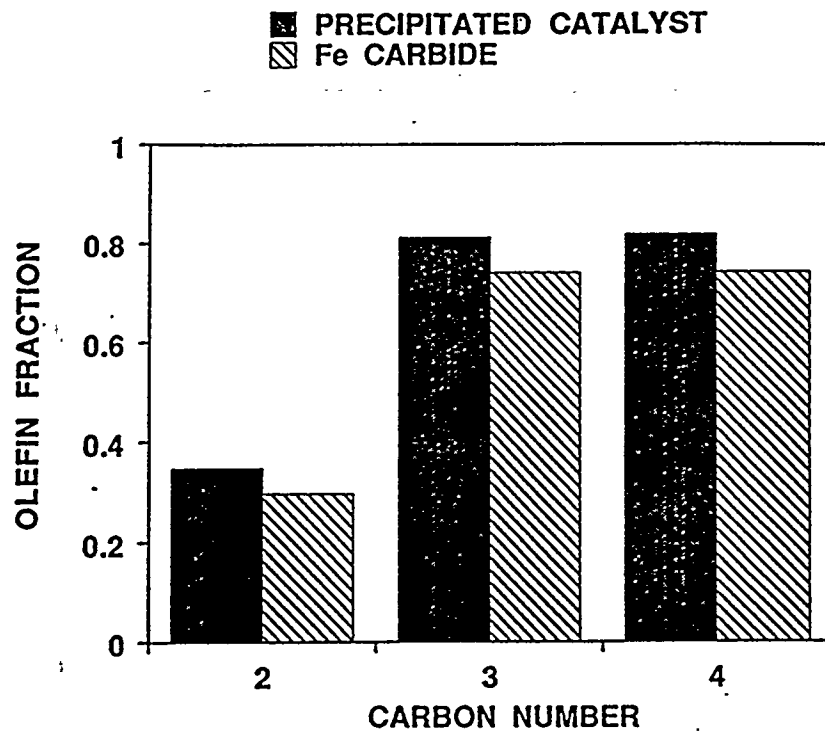


Figure VI.8.5. Comparison of the hydrocarbon production and selectivity at 26% CO conversion for the iron carbide catalyst and the precipitated iron oxide catalyst pretreated with CO.

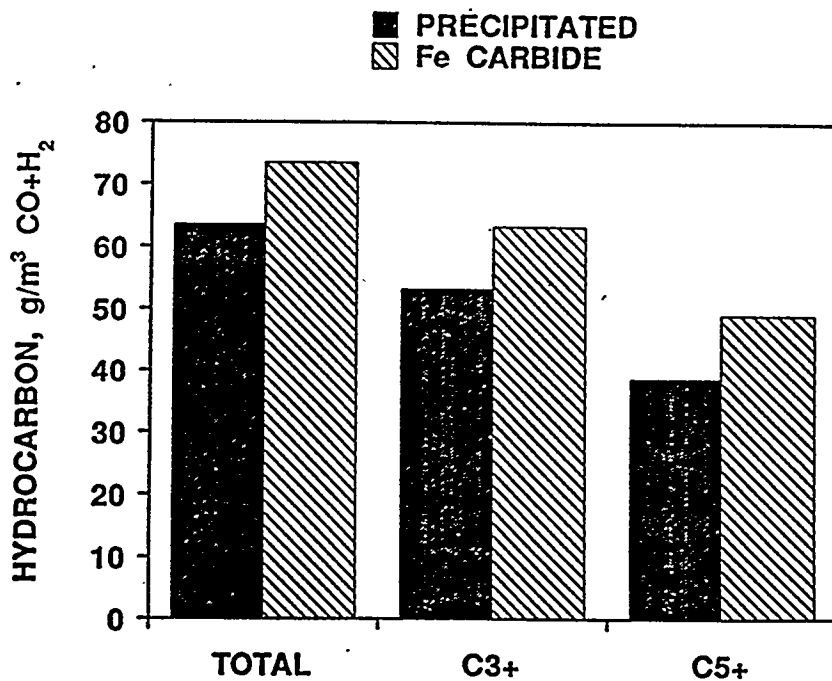


Figure VI.8.6. Comparison of the methane and ethane production at 26% CO conversion for the iron carbide catalyst and the precipitated iron oxide catalyst pretreated with CO.

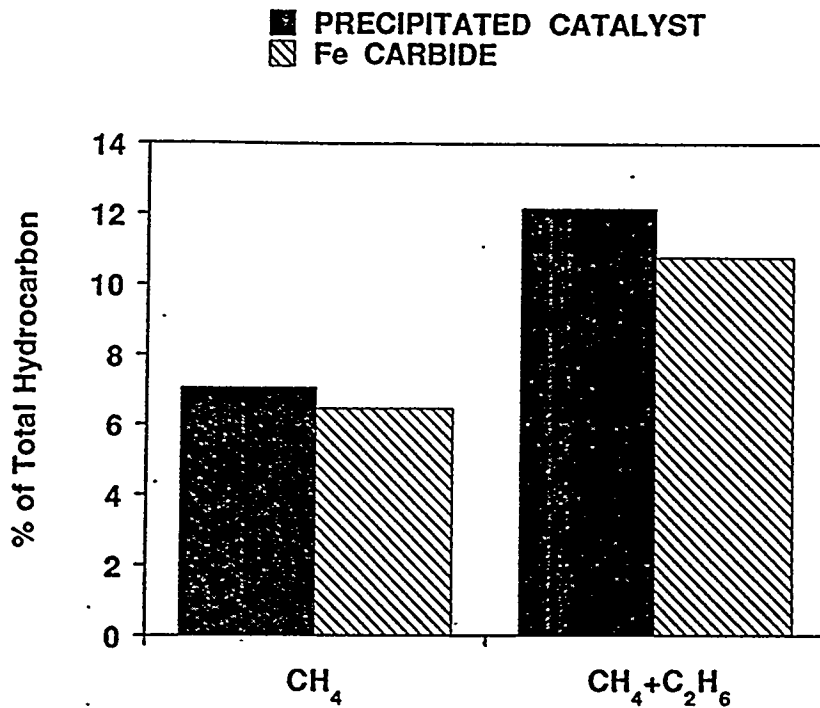


Figure VI.8.7. XRD results for the precipitated iron oxide catalyst at various times of the CO pretreatment and Fischer-Tropsch Synthesis.

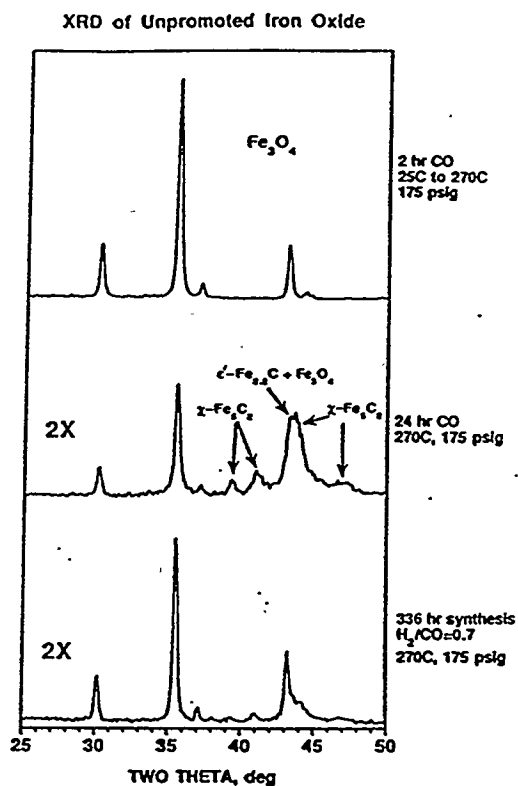


Figure VI.8.8. XRD results for iron carbide catalyst synthesized by laser pyrolysis at various times of the Fischer-Tropsch Synthesis.