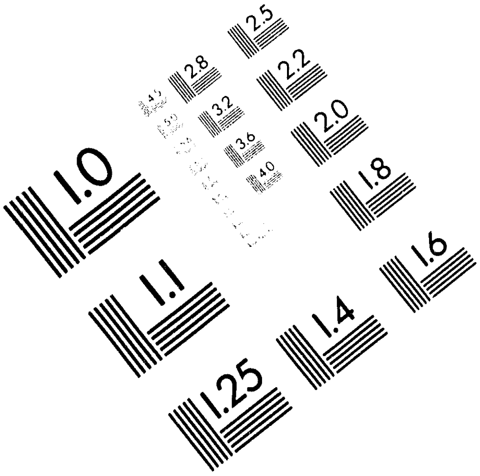

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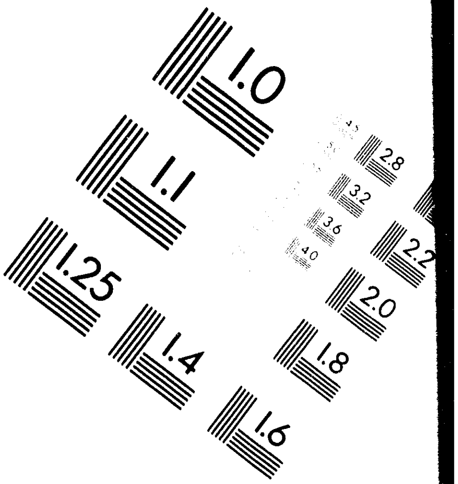

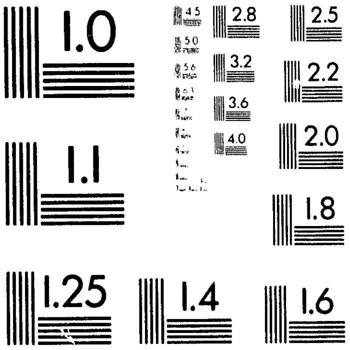

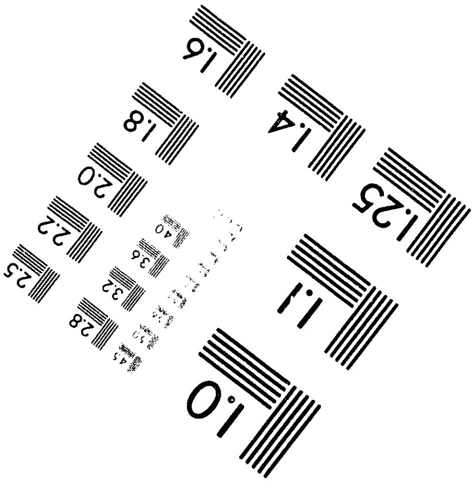

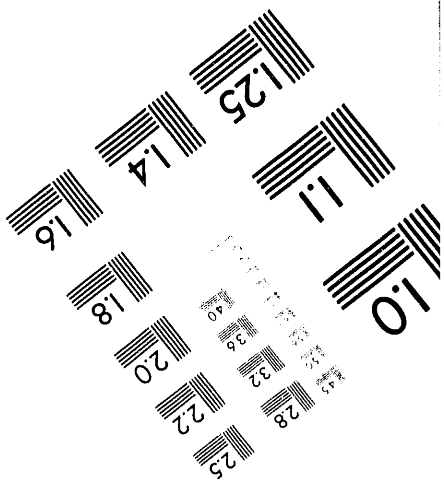

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QUARTERLY TECHNICAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER, 1993

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

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FISCHER-TROPSCH SYNTHESIS AND XRD CHARACTERIZATION OF AN IRON CARBIDE CATALYST SYNTHESIZED BY LASER PYROLYSIS

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INTRODUCTION

Carbides have been implicated as possible reactive species for iron based Fischer-Tropsch catalysts.[1-3] Iron carbides which have been identified during the Fischer-Tropsch Synthesis (FTS) include: χ-Fe_5C_2, ϵ'-$Fe_{2.2}C$, θ-Fe_3C and Fe_7C_3.[4-7] Reducing catalysts to χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ 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.[8-10] Rice et al. have reported that a near stoichiometric θ-Fe_3C catalyst, produced by laser pyrolysis and operating at 270°C, 75 psig and $H_2/CO=2$ had a higher selectivity for olefins and C_5+ 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.[8] Soled et al. reported that the olefin selectivity of a θ-Fe_3C catalyst synthesized by laser pyrolysis is not effected by potassium promotion as are precipitated iron oxide catalysts.[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.

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 $Fe(NO_3)_3 \cdot 9H_2O$ and concentrated NH_4OH at pH 10. The precipitate was thoroughly washed with distilled-deionized H_2O and dried at 120C. The iron carbide catalyst was prepared by pyrolysis of $Fe(CO)_5$ and C_2H_4 with a CO_2 laser using a similar procedure to that reported by Rice et al.[8] The batch of catalyst used in this study was collected in a 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 θ-Fe_3C and Fe_7C_3 with particle sizes <300 Å and surface areas of ~70 m^2/g.

Catalyst slurries consisting of 72.7 g of precipitated catalyst or 12.0 g of iron carbide and 290 g of C_{30} oil were mixed inside a 1 L autoclave operated as a continuous stirred tank reactor (Figure 1). The precipitated catalyst slurry was heated to 270C at 1.5-2.0°C/min under a flow of CO (2.0 nL/hr-g(Fe)). CO pretreatment continued at 270°C for 24 hr. Following pretreatment, hydrogen flow was started to give a H_2/CO ratio of 0.7 with a flow rate of 3.4 nL/hr-g(Fe). The iron carbide catalyst slurry was heated to 270C under CO at 2.0 nL/hr-g(Fe) synthesis gas ($H_2/CO=0.7$) 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_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.

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 (CuKα=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.

RESULTS AND DISCUSSION

Conversion data as a function of time of synthesis for the two catalysts are shown in Figures 2 and 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_2, C_3 and C_4 olefin selectivities at 26% CO conversion (precipitated catalyst-336 hr of synthesis, iron carbide catalyst-122 hr of synthesis) are shown in Figure 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.[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_2-C_4 olefin content of 37% at 72% conversion compared to 86% olefin at 55% conversion for the iron carbide catalyst.[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_3+ (86% vs. 84%) and C_5+ (67% vs. 61%) hydrocarbons (Figure 5). Correspondingly, the iron carbide catalyst produces less methane and ethane than the precipitated catalyst (Figure 6). These hydrocarbon and C_5+ selectivities are similar to those reported earlier.[8-10]

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

$$2H_2 + CO \rightarrow CH_2 + H_2O$$

$$CO + H_2O \rightarrow H_2 + CO_2.$$

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

$$H_2 + 2CO \rightarrow CH_2 + CO_2.$$

The ratio of CO_2 produced to CO converted is 0.5 for this case. The CO_2/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_2.

Characterization

Heating the precipitated catalyst from 25C to 270C (2 hr) under CO rapidly reduced the catalyst to Fe_3O_4 (Figure 7). Further reduction to iron carbides during the CO pretreatment proceeded much more slowly. After 3.5 hr of CO pretreatment at 270C, XRD showed trace amounts of ϵ'-$Fe_{2.2}C$ and χ-Fe_5C_2. After 10 hr at 270C, the carbide phases were more distinct; however, Fe_3O_4 was still the dominant phase. After the completion of the pretreatment, 24 hr at 270C, the catalyst consisted of a mixture of ϵ'-$Fe_{2.2}C$ and χ-Fe_5C_2 with a substantial amount of Fe_3O_4. During the first 2 hr of exposure to synthesis conditions the peaks associated with the ϵ'-$Fe_{2.2}C$ and χ-Fe_5C_2 phases increased in intensity; however, during the remainder of the run, the carbide phases decreased as the intensity of the peaks associated with Fe_3O_4 increased. After 336 hr of synthesis the catalyst had essentially reoxidized to Fe_3O_4.

Similar results were obtained for the iron carbide catalyst (Figure 8). XRD of the catalyst following heat-up to 270C in CO showed predominantly θ-Fe_3C and Fe_7C_3 with a small amount of Fe_3O_4. The Fe_3O_4 peaks grew in intensity during the first 25 hr of synthesis and after 50 hr of synthesis, Fe_3O_4 was the dominant phase. The XRD of the catalyst after 190 hr of synthesis showed only Fe_3O_4.

The oxidation of iron carbides during the Fischer-Tropsch synthesis has been well established.[4,11-13] Synthesis gas is reducing; however, as the concentrations of H_2O and CO_2 increase due to the Fischer-Tropsch and water-gas shift reactions the gas in the reactor becomes oxidizing. A H_2O/H_2 ratio of ~0.02 and a CO_2/CO ratio of ~2 are necessary for Fe_3O_4 to be thermodynamically stable at the synthesis conditions used in this study.[14] The concentration of CO_2 was not high enough to be oxidizing for the iron carbide catalyst; however, the H_2O/H_2 ratio (0.08-0.2) was high enough to oxidize the catalyst to Fe_3O_4. Likewise the H_2O concentration was sufficient to oxidize the precipitated catalyst ($H_2O/H_2=0.2$) as was the CO_2 concentration at the beginning of the run ($CO_2/CO=2.5$).

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

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 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 θ-Fe_3C and Fe_7C_3 at the start of the synthesis; whereas, the CO pretreated catalyst contained the carbides χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$. Exposure to synthesis conditions brought about the oxidation of both catalysts to essentially 100% bulk Fe_3O_4;however, this does not rule out the possibility that the carbides survived on the surface of the catalyst.

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FIGURE LEGEND

Figure 1.	Reactor configuration for 1 L CSTR.
Figure 2.	Synthesis gas conversion data as a function of time of synthesis for the iron carbide catalyst synthesized by laser pyrolysis.
Figure 3.	Synthesis gas conversion data as a function of time of synthesis for the precipitated iron oxide catalyst pretreated with CO.
Figure 4.	Comparison of the C_2, C_3 and C_4 olefin fraction at 26% CO conversion for the iron carbide catalyst and the precipitated iron oxide catalyst pretreated with CO.
Figure 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 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 7.	XRD results for the precipitated iron oxide catalyst at various times of the CO pretreatment and Fischer-Tropsch Synthesis.
Figure 8.	XRD results for iron carbide catalyst synthesized by laser pyrolysis at various times of the Fischer-Tropsch Synthesis.

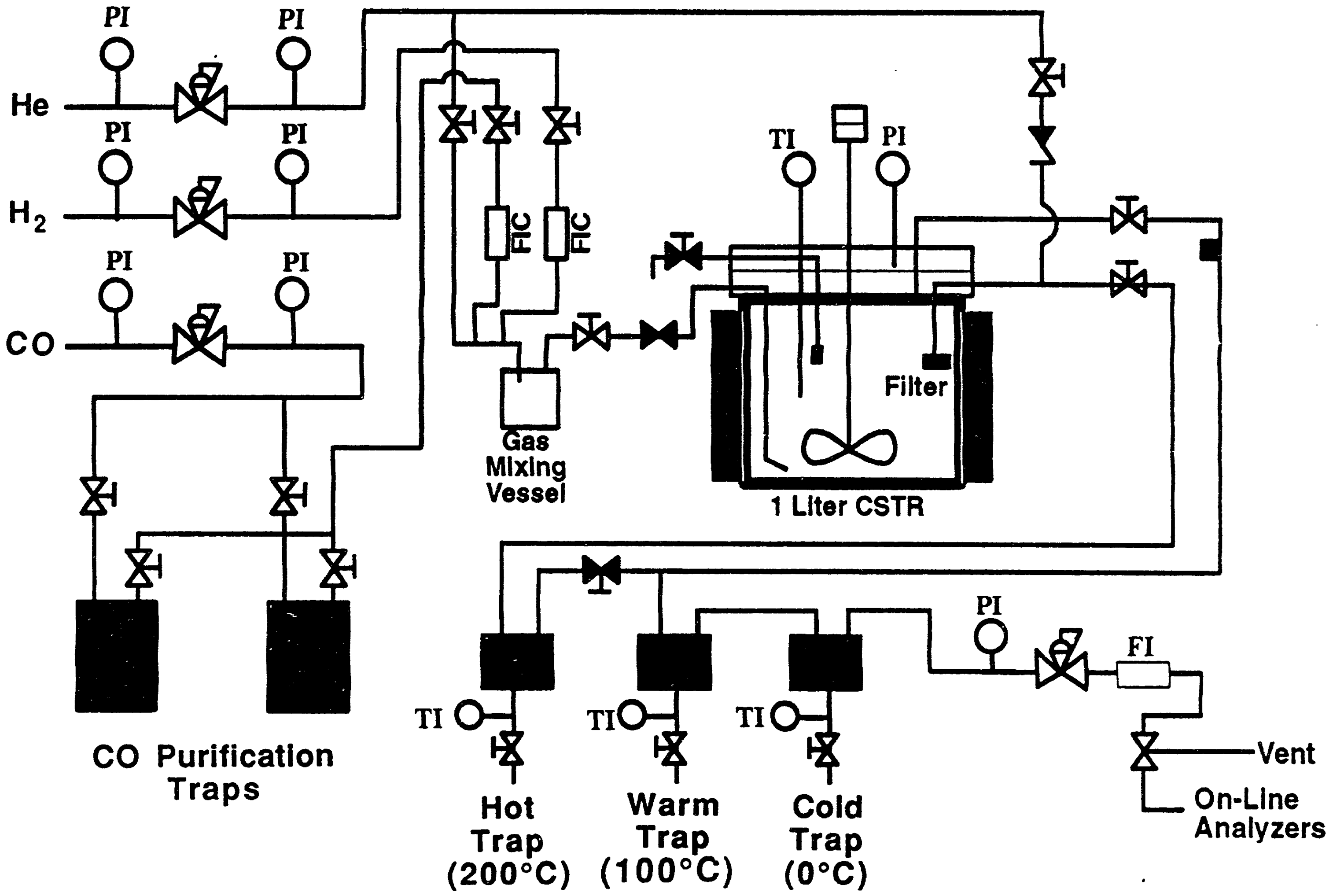

PI
PI
He
PI
PI
H2
PI
PI
CO
CO Purification
Traps
FIC
FIC
Gas
Mixing
Vessel
TI
PI
Filter
1 Liter CSTR
PI
FI
TI
TI
TI
Hot
Trap
(200°C)
Warm
Trap
(100°C)
Cold
Trap
(0°C)
Vent
On-Line
Analyzers

Figure 1

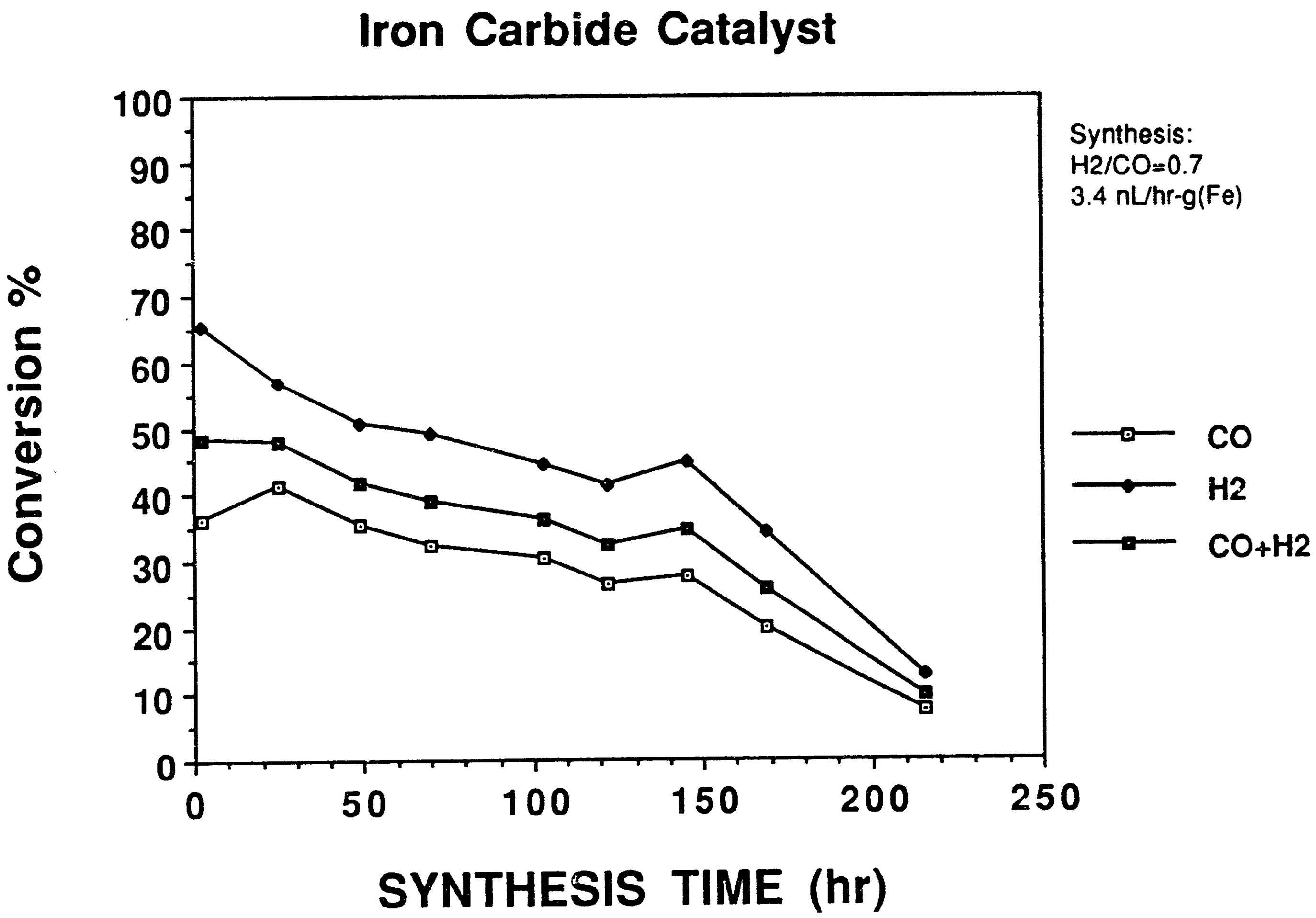
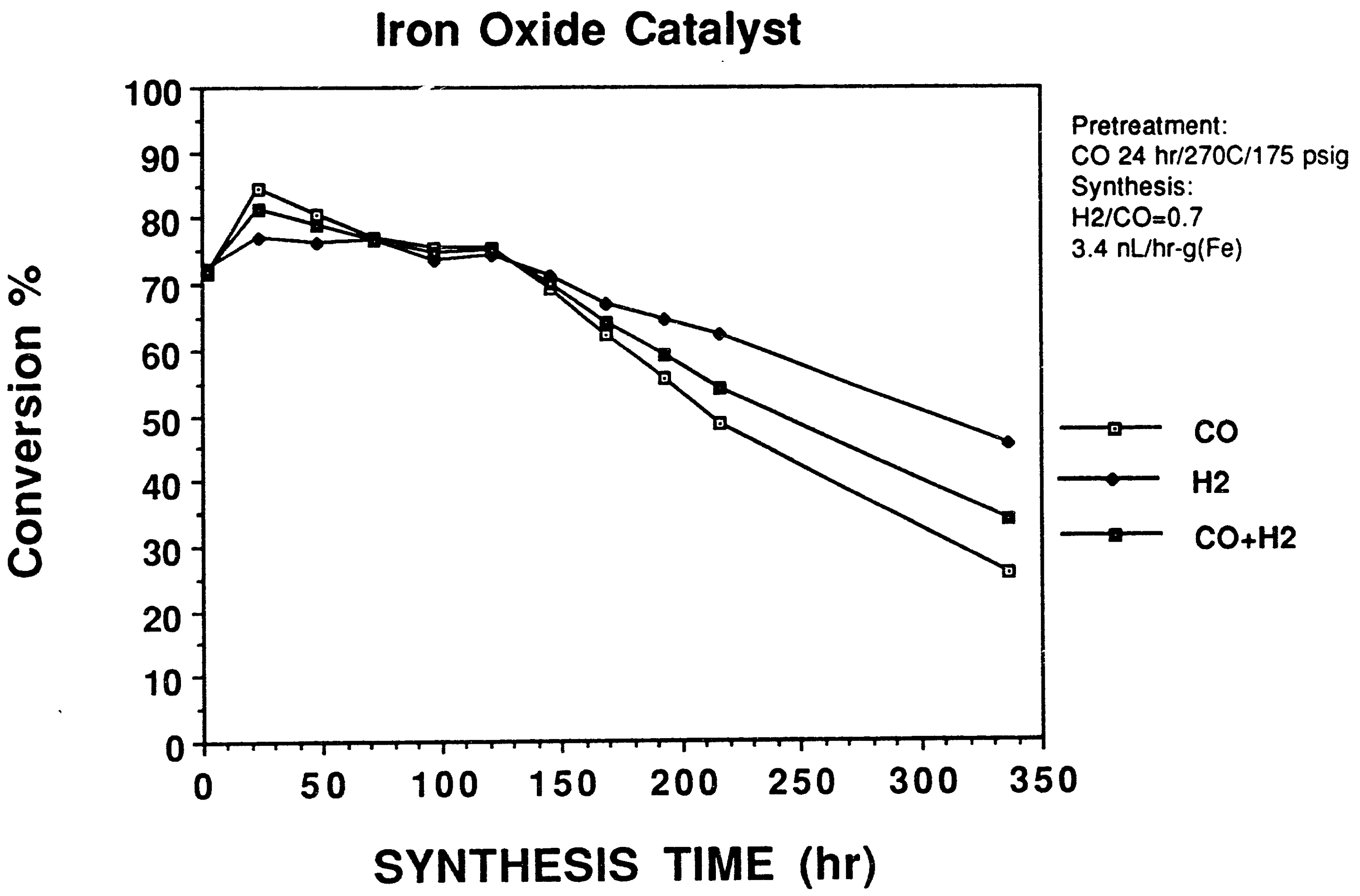
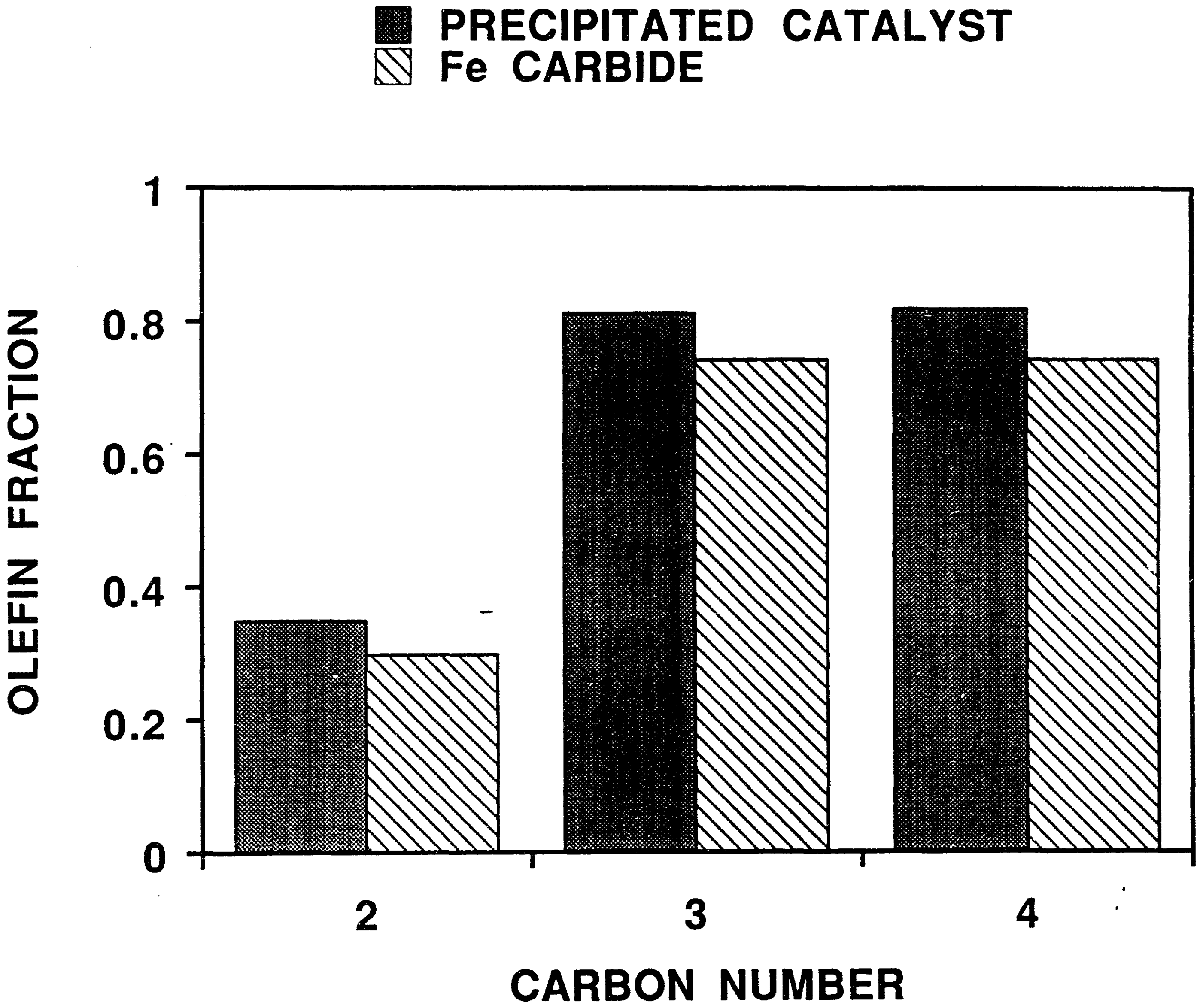

Iron Carbide Catalyst
Conversion %
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
SYNTHESIS TIME (hr)
Synthesis:
H2/CO=0.7
3.4 nL/hr-g(Fe)
CO
H2
CO+H2

Figure 2



Iron Oxide Catalyst
Conversion %
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
350
SYNTHESIS TIME (hr)
Pretreatment:
CO 24 hr/270C/175 psig
Synthesis:
H2/CO=0.7
3.4 nL/hr-g(Fe)
CO
H2
CO+H2

Figure 3



PRECIPITATED CATALYST
Fe CARBIDE
1
0.8
0.6
0.4
0.2
0
OLEFIN FRACTION
2
3
4
CARBON NUMBER

Figure 4

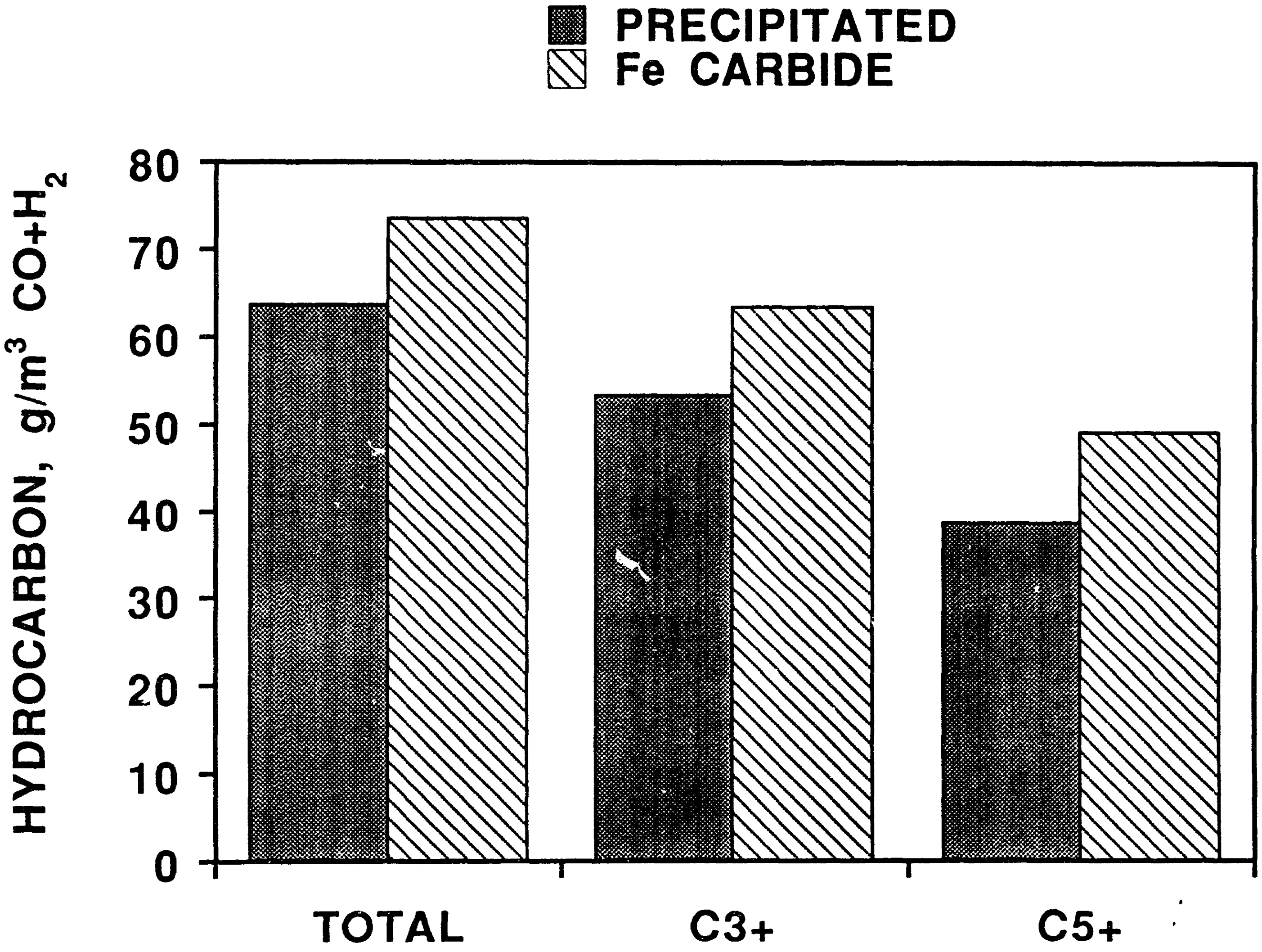
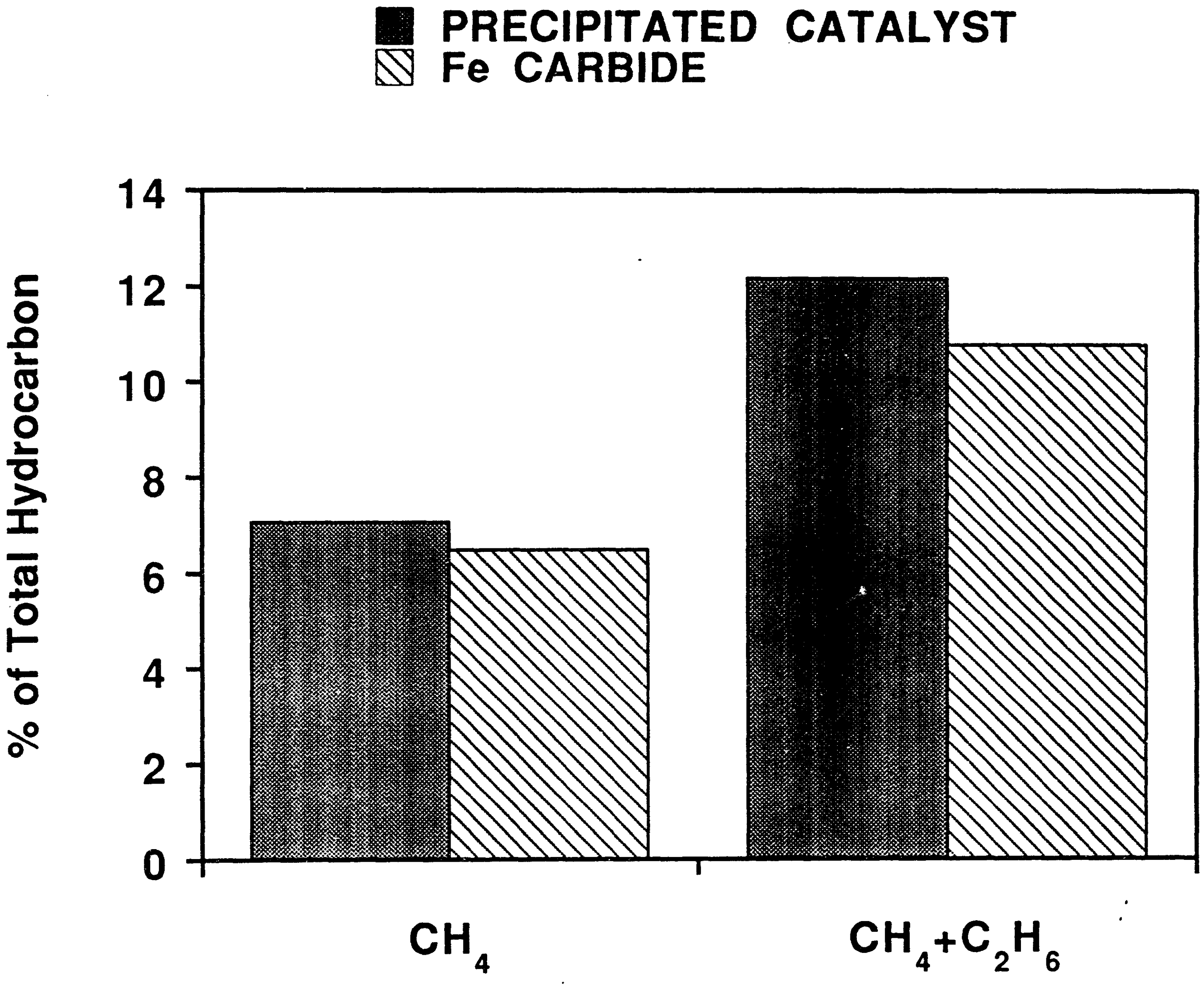

▩ PRECIPITATED
▧ Fe CARBIDE
HYDROCARBON, g/m^3 CO+H_2
80
70
60
50
40
30
20
10
0
TOTAL
C3+
C5+

Figure 5



PRECIPITATED CATALYST
Fe CARBIDE
% of Total Hydrocarbon
0
2
4
6
8
10
12
14
CH_4
$CH_4+C_2H_6$

Figure 6

XRD of Unpromoted Iron Oxide

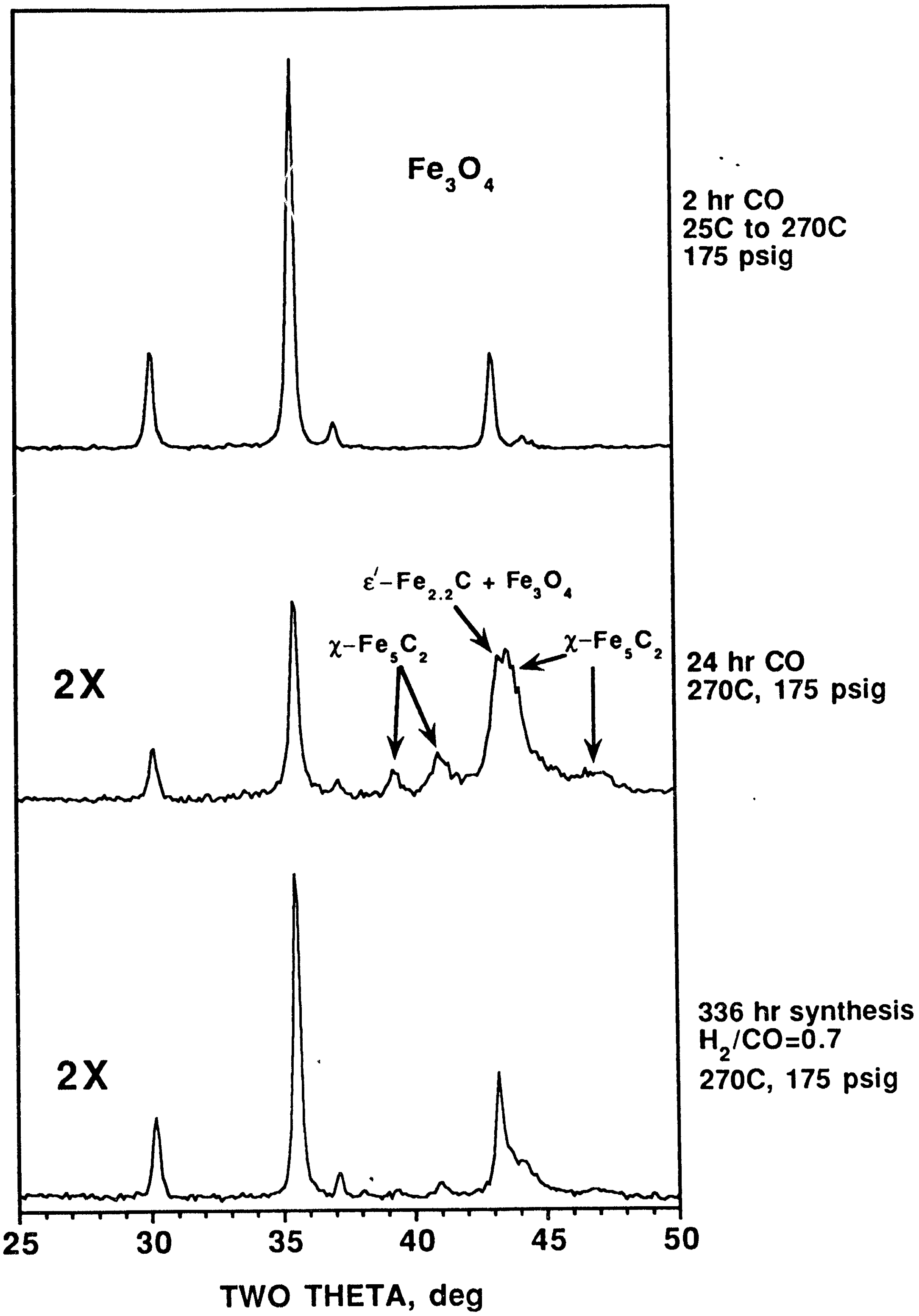


Figure 7

XRD of Iron Carbide Catalyst

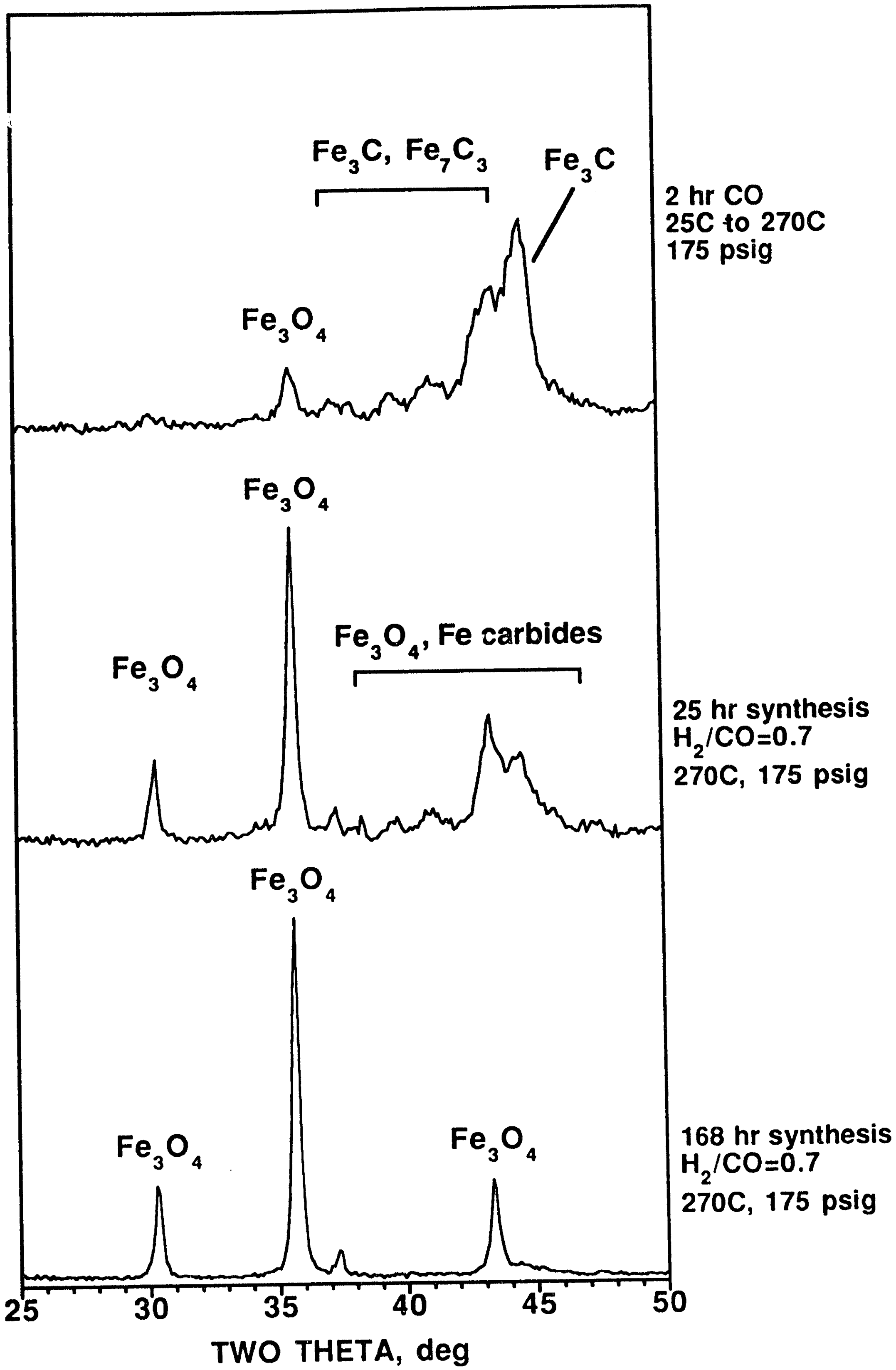


Figure 8

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