DOE/PC/94055--T1

QUARTERLY TECHNICAL PROGRESS REPORT

Technology Development for Iron Fischer-Tropsch Catalysis - Period ending

December 31, 1994

Contract No.: DE-AC22-91PC94055

Contractor: University of Kentucky Research Foundation
Kinkead Hall
Lexington, KY 40506-0057

Starting Date: September 28, 1994

Ending Date: September 27, 1997

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SYNTHESIS GAS ACTIVATION OF A PRECIPITATED IRON FISCHER-TROPSCH CATALYST

INTRODUCTION

Fischer-Tropsch catalysts must undergo a pretreatment in order to be active. In the case of Co and Ru catalysts, activation is rather straight forward; reduction to zero-valent Co or Ru with hydrogen is sufficient. Activation of iron Fischer-Tropsch catalysts is not as facile. Fused magnetite catalysts must be activated with H_2 at temperatures in excess of 400°C in order to obtain a high surface area; activation in synthesis gas or CO in ineffective.[1] Precipitated catalysts have been reported to be successfully activated using CO, H_2 and synthesis gas.[2,3] Several studies have shown CO to be the most effective activation gas for precipitated iron catalysts;[2,4,5] however, Kölbel reported high activity using synthesis gas activation in his slurry phase demonstration plant studies.[3] Synthesis gas activation may yield high activity but seems to depend strongly on the conditions employed, including: temperature, pressure and duration. Hydrogen activation is fairly tricky because zero-valent iron is generated; zero-valent iron is susceptible to sintering so the reduction must be performed at low temperatures with a high linear gas flow to quickly remove water generated during the reduction.[1] Bukur reports long term activity to be similar for H_2 and CO activated catalysts; however, while he reports high initial activity for a catalyst activated with synthesis gas, the stability is poor.[2] In our studies we have found that CO activation at 270°C, 175 psig for 24 hr consistently gives good results; several catalysts have achieved CO conversions in excess of 90% at 270°C, 175 psig and a space velocity ($H_2/CO=0.7$) of 3.4 nL/hr-g(Fe). As part of our comprehensive study to maximize the activity of iron based precipitated Fischer-Tropsch catalysts, we are currently attempting to optimize the activation procedure. Although we are able to achieve high activity using CO pretreatment, the catalysts tend to deactivate suddenly and rapidly after 500 hr of synthesis. Kolbel reports high CO conversion comparable to our results at a lower gas flow (2.4 vs. 3.4 nL/hr-g(Fe)); however, he achieved greater stability with conversions reported to be 90% after 1400 hr.[3] One possibility for Kolbel's higher stability could be due to the activation procedure. Herein are reported the initial results of a study to optimize the catalyst composition and the operating conditions for the iron based slurry phase Fischer-Tropsch synthesis when synthesis gas activation is utilized.

EXPERIMENTAL

The catalyst used in this study was prepared by continuous precipitation of ferric oxyhydroxide from 1.17 M $Fe(NO_3)_3 \cdot 9H_2O$ by adding concentrated NH_4OH to produce a suspension with a pH of ~9.5. The catalyst was promoted with silicon by adding hydrolyzed $Si(OC_2H_5)_4$ to the ferric nitrate solution. Copper promotion was accomplished by impregnating the dried catalyst with aqueous $Cu(NO_3)_2 \cdot 2.5H_2O$ by the incipient wetness technique. Promotion with potassium was accomplished by adding the appropriate amount of potassium *t*-butoxide to the catalyst oil slurry in the Fischer-Tropsch reactor. The nominal catalyst compositions for the catalysts used in this study, given as atomic % relative to iron metal, are 100Fe/4.4Si/0.71K and 100Fe/4.4Si/0.71K/2.6Cu.

Catalysts were tested in a one liter autoclave operated as a continuous stirred tank reactor. The catalysts were suspended in a hydrocarbon oil supplied by Ethyl which has a carbon number range of about C_{25}-C_{30}. A schematic of the reactor system is shown in Figure 1. The H_2 and CO feed gas flow rates were controlled individually by mass flow controllers supplied by Brooks Instruments. The H_2/CO feed ratios were consequently controlled by changing the flow rates of the appropriate gas. The resulting synthesis gas was delivered to the catalyst slurry through a 1/8" i.d. dip tube that ran to the bottom of the reactor below the impeller blade. The reactor was equipped with three product traps maintained at nominal temperatures of 200°C, 60°C and 0°C. The 200°C trap was connected to a line fitted with a 0.5 μm filter. The filter was placed inside the reactor approximately 2" from the top. This allowed for removal of accumulated wax inside the reactor. Uncondensed effluent was vented to atmospheric pressure and was directed to on-line gas analyzers. A Carl gas analyzer was used to analyze for C_1-C_4 hydrocarbons, CO, H_2, and CO_2; a Hewlett-Packard 5790 GC equipped with a porpack-Q column was used for analysis of C_4-C_9 hydrocarbons.

The reactor was also fitted with a 1/8" dip tube equipped with a high temperature valve which enabled catalyst slurry samples to be removed from the reactor periodically during the pretreatment and synthesis, and these were used for characterization studies.

Catalysts were activated with synthesis gas having a molar ratio of $H_2/CO=0.7$. Activation was carried out at 175 psig with a space velocity of 3.4 nL/hr-g(Fe). Following the start of synthesis gas flow, the temperature of the reactor was increased to 270°C at a rate of 2°C/min. These conditions were maintained throughout the runs. Synthesis gas conversions were determined by measuring the exit stream flow rate with a bubble film flow meter and by gas chromatography of the exit stream.

Powder X-ray diffraction patterns of the catalysts were obtained using a Philips ADP 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.

RESULTS AND DISCUSSION

Activation of the 100Fe/4.4Si/0.71K catalyst with synthesis gas was unsuccessful. Carbon monoxide conversion slowly increased to 12% and then stabilized after 92 hr. Activity and selectivity data are shown in Table 1. In a previous study, this catalyst showed high activity and productivity when pretreated with CO at 270°C, 175 psig for 24 hr: carbon monoxide conversions were found to exceed 90% and total hydrocarbon yields surpassed 170 g/m^3-syngas for up to 300 hr of synthesis.

It was decided to determine the affect that a CO treatment would have on the inactive catalyst. After 92 hr of synthesis, the hydrogen flow was stopped and the catalyst was exposed to CO at 270°C, 175 psig, 2.0 L/hr-g(Fe) for 24 hr. Following the CO treatment, H_2 flow was resumed and the activity of the catalyst was found to rapidly increase to 84% CO conversion within 26 hr. The ultimate activity of the catalyst was similar to when it was pretreated with CO (Figure 2). The selectivity and productivity were also similar as seen by the data in Table 1.

Powder X-ray diffraction analysis suggests that the catalyst was reduced to Fe_3O_4 during activation with synthesis gas; however, only a small amount of χ-Fe_5C_2 was formed. Treatment of the catalyst with CO for 24 hr increased the χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ content at the expense of the Fe_3O_4 (Figure 3). During the synthesis following the CO treatment, the peaks corresponding to ϵ'-$Fe_{2.2}C$ increased while the χ-Fe_5C_2 seemed to remained constant. Peaks corresponding to Fe_3O_4 were the most intense throughout the run. These findings are very similar to those found when the catalyst was pretreated with CO. Based on these preliminary results, it appears that the increase in activity when the inactive catalyst was treated with CO can be correlated with the formation of χ-Fe_5C_2 and/or ϵ'-$Fe_{2.2}C$.

Promotion with Cu is considered to aid the reduction of iron Fischer-Tropsch catalysts and would, based on the above, seem likely to increase the activity of the 100Fe/4.4Si/0.71K catalyst when activated in synthesis gas. Figure 4 shows the activity of the 100Fe/4.4Si/2.6Cu/0.71K catalyst following activation with synthesis gas. The activity was substantially higher due to the Cu promotion; however, the catalyst never achieved the activity of the CO pretreated 100Fe/4.4Si/0.71K catalyst. It is interesting that the activity increased steadily from 26% to 51% CO conversion during the 200 hr the catalyst was run. Selectivity data is presented in Table 1. In general CH_4 and C_2H_6 selectivity should be low at low CO conversion; however, promotion with Cu seemed to increase the CH_4 and C_2H_6 selectivity to the same level as when the catalyst was run at high conversion. Powder X-ray diffraction data show more intense χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ carbide peaks for the Cu promoted catalyst than the catalyst with no Cu (Figure 5). This tends to support the finding that some iron carbide must be present for reasonable activity to be achieved. During the run, the amount of χ-Fe_5C_2 seemed to remain constant; however, the ϵ'-$Fe_{2.2}C$ peaks increased. It is tempting to correlate the increase in activity during the run with the increase in ϵ'-$Fe_{2.2}C$; however, a previous Mössbauer study with the CO pretreated 100Fe/4.4Si/0.71K catalyst showed no correlation between the amount of ϵ'-$Fe_{2.2}C$ or χ-Fe_5C_2 and activity.

Bukur reported high activity when synthesis gas activation ($H_2/CO=0.68$ at 280°C, 1 atm) was used on a precipitated iron catalyst promoted with K and Cu.[2] In addition, Soled et al. report high activity for a Cu/K promoted iron-zinc catalyst activated in the slurry phase with a synthesis gas with $H_2/CO=2.0$ at 270°C and 75 psig.[6] Kölbel successfully activated a K/Cu promoted precipitated iron catalyst with synthesis gas ($H_2/CO=0.67$ to 0.77) in a slurry phase demonstration plant.[3] The catalyst was treated with the synthesis gas at a formation temperature ranging from 15°C to 30°C above the final operating temperature. The CO_2 production was monitored and the activation was considered complete a few hours after the CO_2 production reached its asymptotic limit. The temperature of the reactor was decreased to the operating temperature and the synthesis was begun. Kölbel considered the formation temperature to be critical; if it is too high the catalyst will deactivate due to carbonization and if it is too low the catalyst will not activate. It is possible that the activation temperature used in the present study was too low to completely activate the catalysts. It is also possible that the presence of silicon could have had a detrimental affect on the activation. Bukur reports that silica inhibits the reduction of Fe_2O_3 to iron carbides by CO.[7] A similar affect would be expected with synthesis gas.

CONCLUSION

Activation with synthesis gas at 270°C and 175 psig ($H_2/CO=0.7$) is ineffective for a precipitated catalyst with molar composition of 100Fe/4.4Si/0.71K. The low activity achieved by synthesis gas activation may be related to the lack of bulk χ-Fe_5C_2 and/or ϵ'-$Fe_{2.2}C$ as seen by XRD. Promotion with Cu increased the extent of reduction of the catalyst and thereby substantially increased the activity of the catalyst when activated in synthesis gas; however Cu promotion did not increase the activity to the same level as when the catalyst is activated with CO. Promotion with silicon may inhibit the reduction of the catalyst to an active state when synthesis gas is used during the activation procedure. Future efforts will focus on the optimization of activation conditions, ie. temperature, pressure and duration, when synthesis gas is utilized. In addition, synthesis gas activation will be performed on catalysts with the compositions, 100Fe/0.71K and 100Fe/2.6Cu/0.71K in order to identify the affect of silicon on activation.

REFERENCES

1. Dry, M. E., *in Catalysis: Science and Technology* (J. R. Anderson and M. Boudart, Eds.), Vol 1. Springer-Verlag, New York, 1981.
2. Bukur, D. B., Lang X., Rossin, J. A., Zimmerman, W. H., Rosynek, M. P., Yeh, E. B., and Li, C., Ind. Eng. Chem. Res. **28**, 1130, (1989).
3. Kőlbel, H. and Ralek, M., *Catal. Rev.-Sci. Eng.* **21**, 225 (1980).
4. Huang, C. S., Xu, L., and Davis, B. H. *Fuel Sci. Technol. Int.* **11**, 639 (1993).
5. Huang, C. S.,Ganguly, B., Hufman, G. P., Huggins, F. E. and Davis, B. H. *Fuel Sci. Technol. Int.* **11**, 1289 (1993).
6. Soled, S. L., Miseo, S., Iglesia, E., Fiato, R. A., 1992. U.S. Patent 5,100,856.
7. Bukur, D. B., Lang, X., Mukesh, D., Zimmerman, W. H., Rosynek, M. P. and Li, C., *Ind. Eng. Chem. Res.* **29**, 1588 (1990).

Table 1

Catalysts

	100Fe/4.4Si/0.71K			100Fe/4.4Si/0.71K			100Fe/4.4Si/2.6Cu/0.71K			
Activation Gas	CO			CO + H_2/CO[a]			CO + H_2			
Time of Synthesis, Hr.	71	263	454	92	168	449	3.5	68	137	187
CO Conversion, %	93	89	82	12	88	82	26	36	44	52
HC Production, g/m^3-CO + H_2										
Total	175	166	156	25	170	150	55	70	86	100
C_3^+	149	136	127	20	149	126	48	58	72	84
Selectivity, Mol%										
CH_4	7.3	8.6	8.7	9.4	6.0	8.9	5.3	7.9	8.5	8.8
$CH_4 + C_2H_6$	12.8	15.5	15.7	12.0	10.1	13.4	8.4	11.6	12.3	13.3
CO_2	49	49	48	43	48	50	43	48	47	47
Olefin Selectivity, Mol%										
C_2	9.7	8.4	10.6	73	16	15	40	44	36	27
C_3	56	52	58	91	62	62	82	84	81	75
C_4	69	65	72	84	74	68	72	80	78	74
1-Butene/Total Butene, Mol%	38	36	54	93	53	59	72	87	84	80

[a] Treated with CO + H_2 (H_2/CO = 0.7) for first 92 hrs., followed by 21 hrs of CO and then CO + H_2 at 270°C, 175 psig.

FIGURE LEGEND

Figure 1.	Schematic of the slurry phase reactor system.
Figure 2.	Comparison of the CO conversion vs. time of synthesis for the 100Fe/4.4Si/0.71K catalyst when activated in CO and $CO+H_2$ ($H_2/CO=0.7$) at 270°C, 175 psig.
Figure 3.	Comparison of X-ray diffractograms for 100Fe/4.4Si/2.6Cu/0.71K catalyst after (a) 92 hr of synthesis gas activation and (b) following 21 hr of CO exposure at 270°C, 175 psig (b).
Figure 4.	Activity vs. time of synthesis for the 100Fe/4.4Si/2.6Cu/0.71K catalyst activated with synthesis gas ($H_2/CO=0.7$) at 270°C, 175 psig.
Figure 5.	Comparison of X-ray diffractograms of (a) 100Fe/4.4Si/0.71K catalyst after 92 hr of synthesis gas activation and (b) 100Fe/4.4Si/2.6Cu/0.71K catalyst after 112 hr of synthesis gas activation.

Figure 1

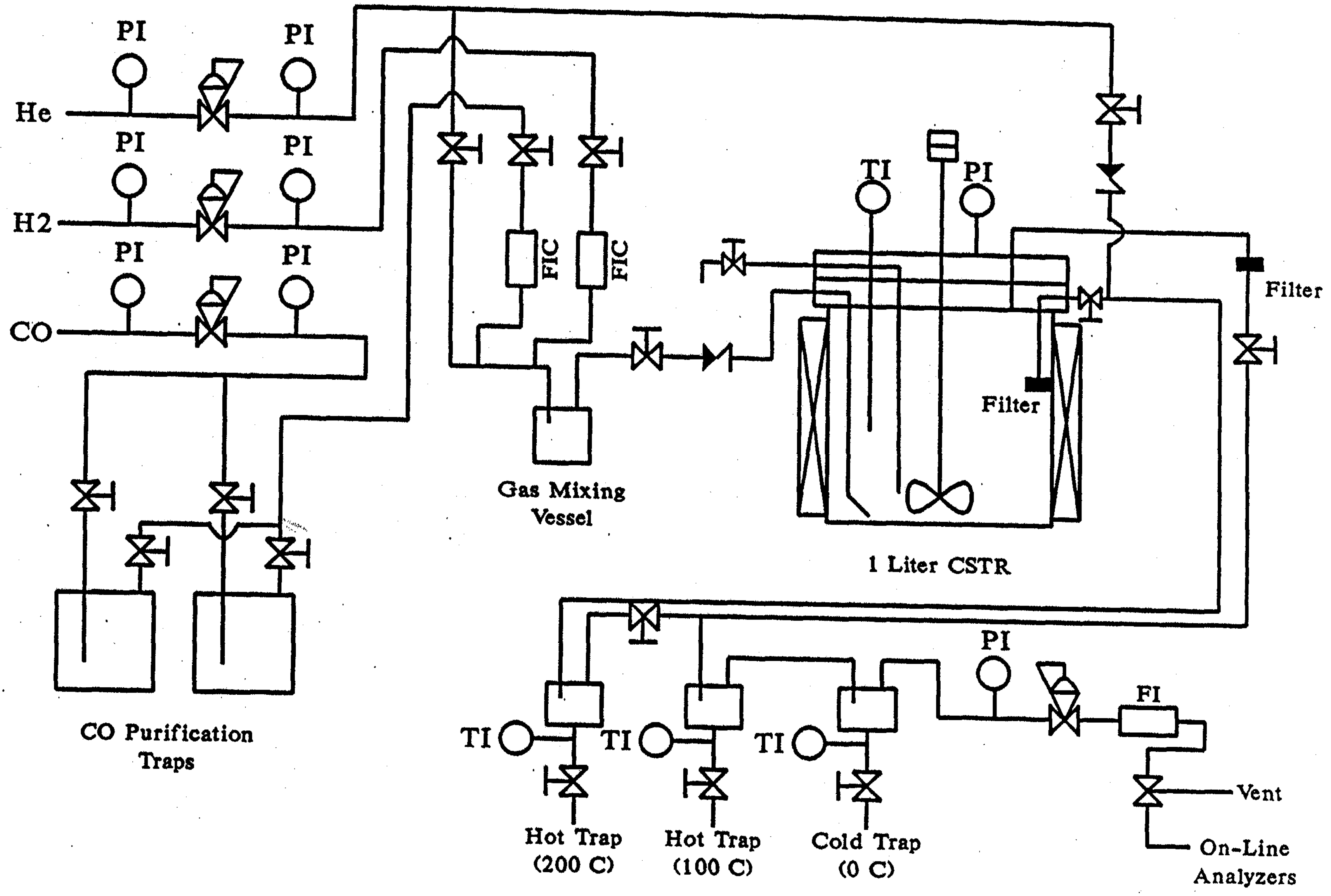

PI
PI
He
PI
PI
H2
PI
PI
CO
FIC
FIC
Gas Mixing
Vessel
CO Purification
Traps
TI
PI
Filter
Filter
1 Liter CSTR
PI
FI
TI
TI
TI
Vent
On-Line
Analyzers
Hot Trap
(200 C)
Hot Trap
(100 C)
Cold Trap
(0 C)

Figure 2

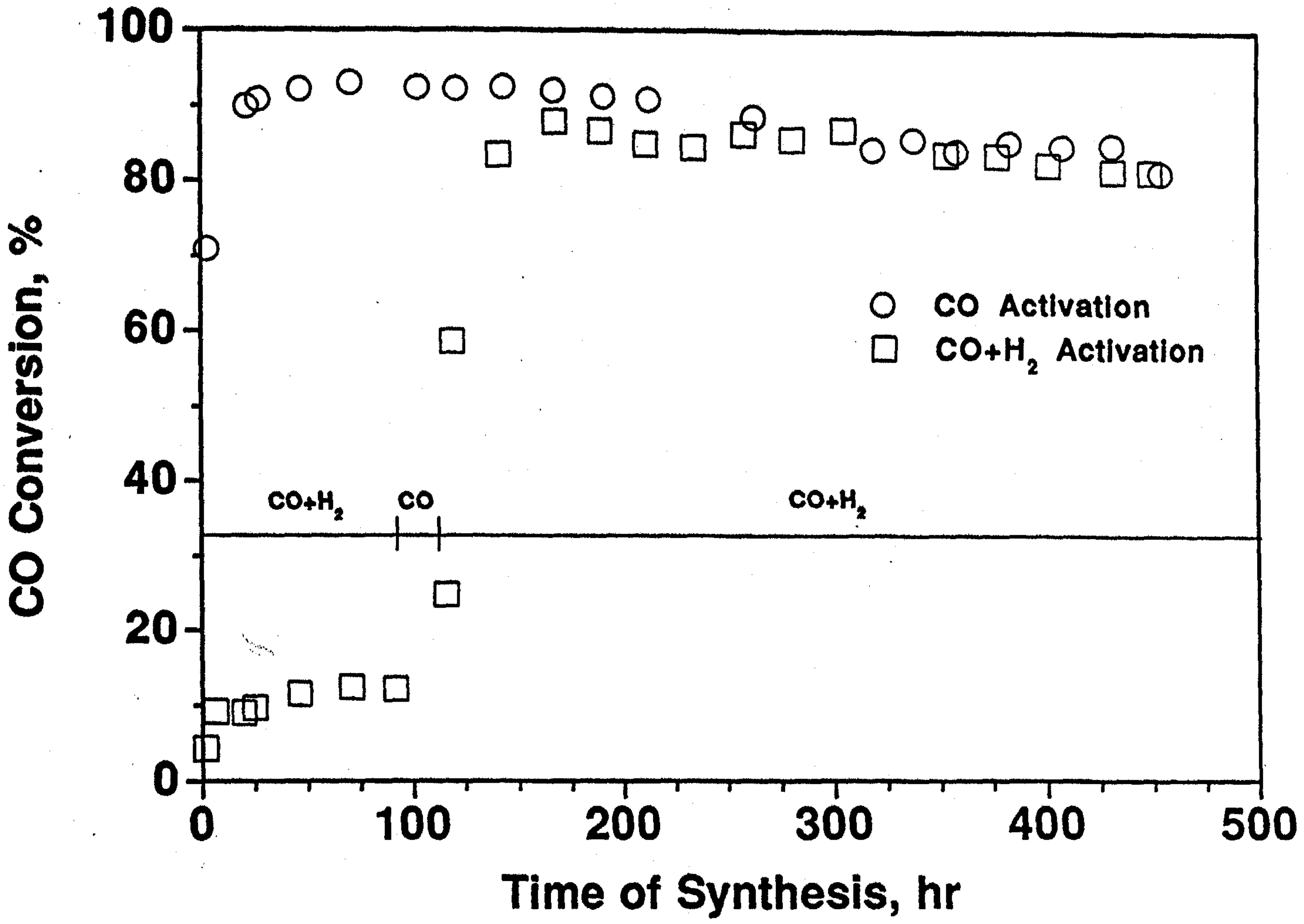
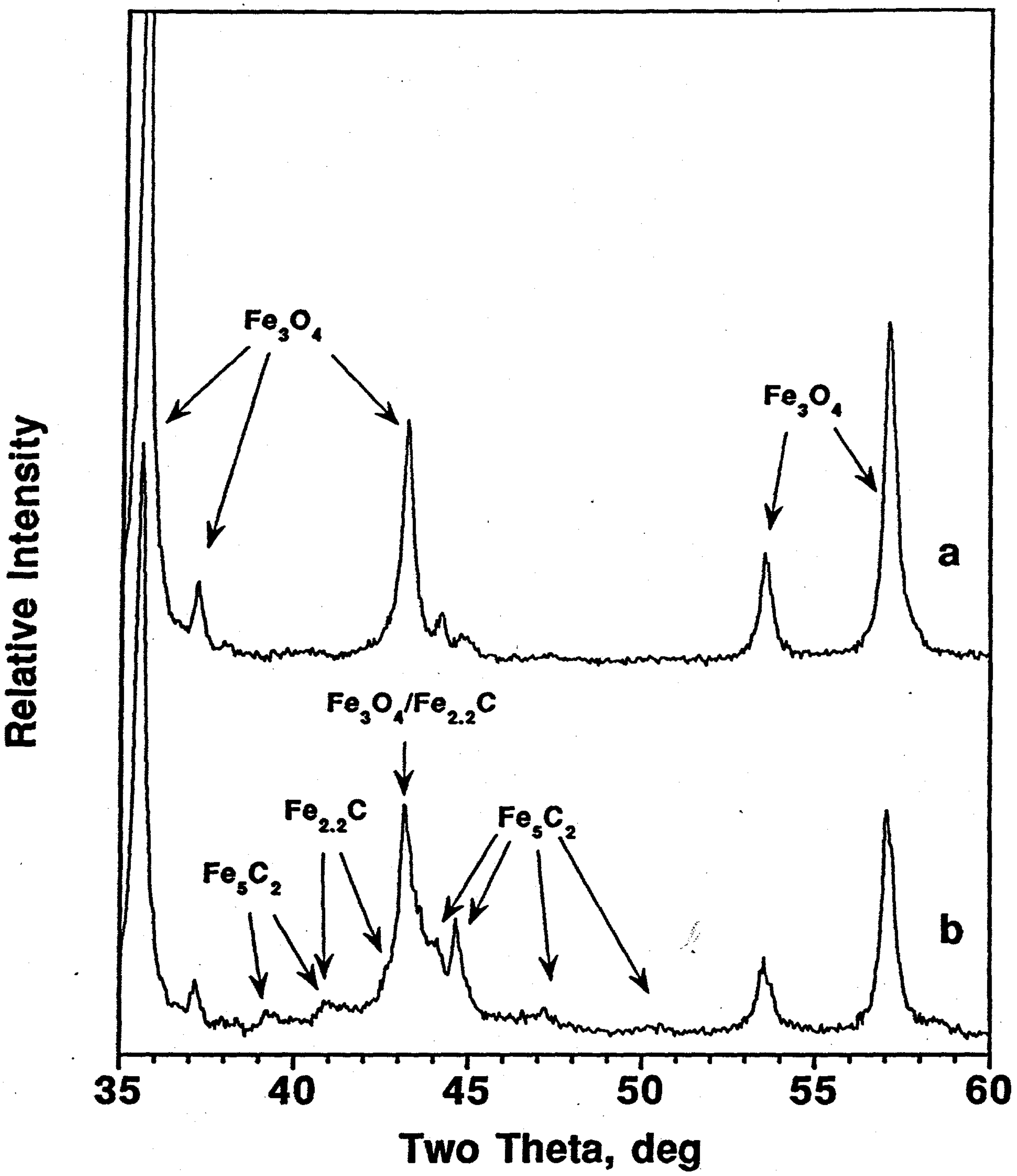

100
80
60
40
20
0
CO Conversion, %
0
100
200
300
400
500
Time of Synthesis, hr
CO+H₂
CO
CO+H₂
○ CO Activation
□ CO+H₂ Activation

Figure 3



Relative Intensity
Fe$_3$O$_4$
Fe$_3$O$_4$
a
Fe$_3$O$_4$/Fe$_{2.2}$C
Fe$_{2.2}$C
Fe$_5$C$_2$
Fe$_5$C$_2$
b
35
40
45
50
55
60
Two Theta, deg

Figure 4

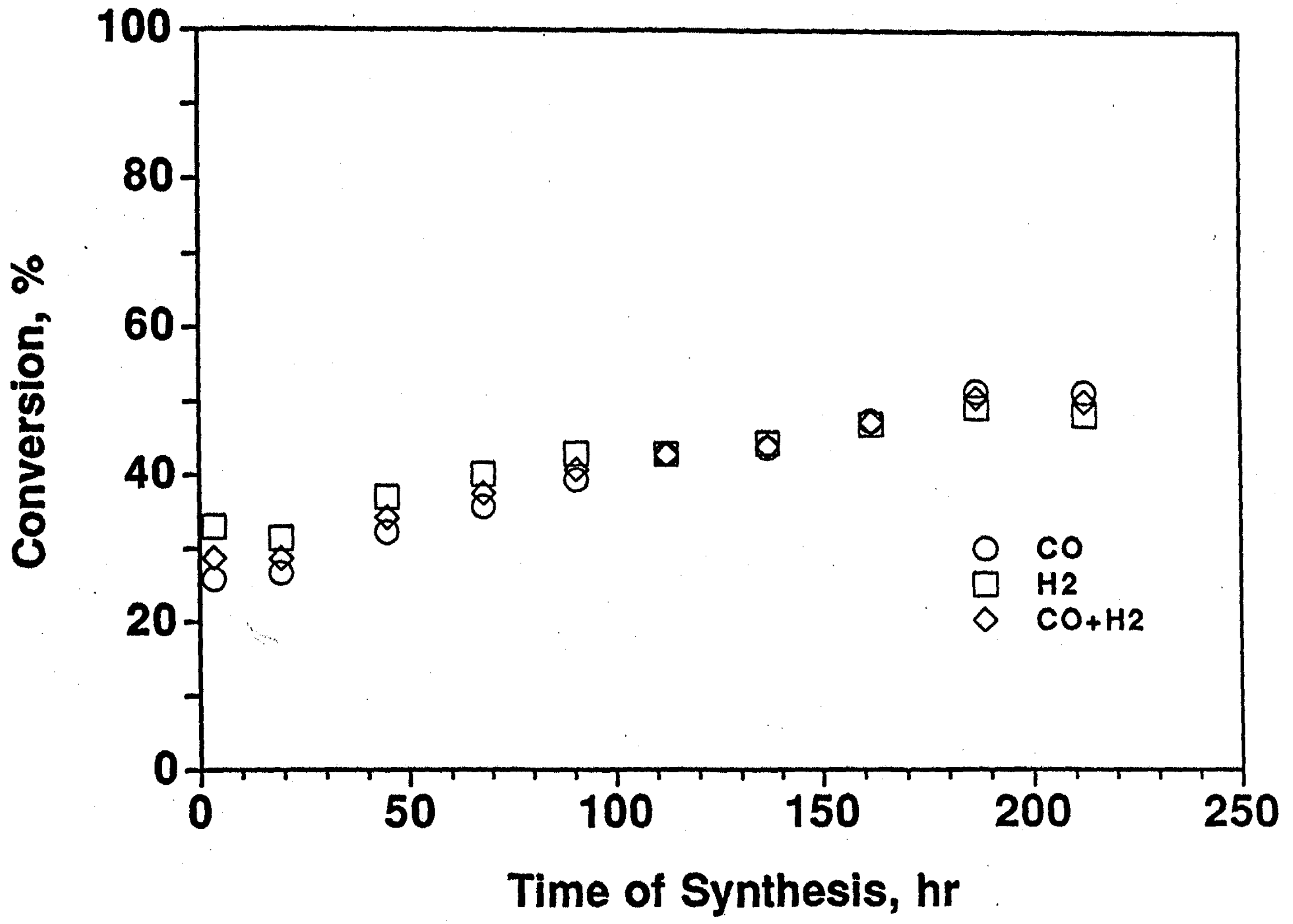
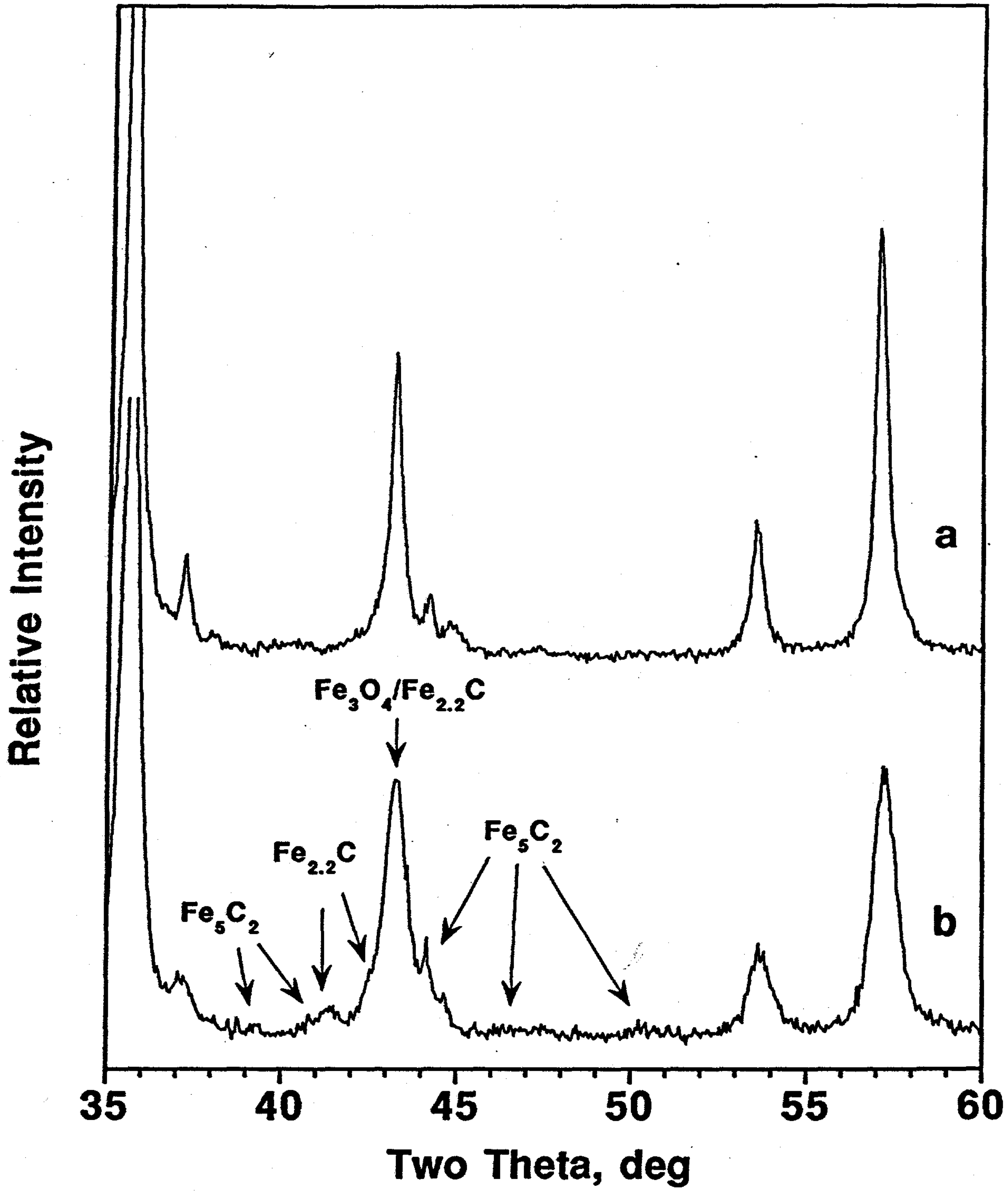

100
80
60
40
20
0
Conversion, %
0
50
100
150
200
250
Time of Synthesis, hr
CO
H2
CO+H2

Figure 5



Relative Intensity
a
b
Fe$_3$O$_4$/Fe$_{2.2}$C
Fe$_{2.2}$C
Fe$_5$C$_2$
Fe$_5$C$_2$
35
40
45
50
55
60
Two Theta, deg