Executive Summary

UC/B

A series of catalysts consisting of Fe, Zn, K and Cu have been prepared by coprecipitation of Zn and Fe hydrous oxides at Zn/Fe atomic ratios from 0 to 0.4. After treatment in dry air at 350^oC, the resulting porous mixed oxides were promoted with 2 at.% K and 1 at.% Cu and calcined at 400 ^oC. Powder X-ray diffraction measurements show that rhombohedral corundum-type Fe_2O_3 structures form in samples with Zn/Fe ratios less than 0.2, and a cubic spinel-type $ZnFe_2O_4$ forms in samples with a Zn/Fe ratio of 0.4. Both Fe_2O_3 and $ZnFe_2O_4$ phases were detected at intermediate Fe/Zn ratios. For samples calcined at low temperature (350 ^oC), the BET surface area of Fe_2O_3 decreases slightly with the addition of a small amount of Zn, but it increases as further increases in Zn content lead to $ZnFe_2O_4$ structures. At the higher calcination temperature (400 ^oC) required to decompose carbonate and nitrate precursors, the addition of Zn, however, leads to significant stabilization of Fe_2O_3 surface areas at all Zn loadings. It appears that the $ZnFe_2O_4$ phase resists sintering during calcination at higher temperatures, and that its effect becomes increasingly critical as the required calcination temperature increases.

Thermodynamic calculations of the phase diagram for the Fe_3C-Fe-C system showed that carburization of Fe oxides with CH_4/H_2 mixtures leads to the formation of oxygen and graphite free carbide only within a narrow range of temperatures and CH_4/H_2 ratios. However, carburization of Fe oxides in this composition-temperature range gave Fe carbides with significant residual Fe metal. Fe oxide reduction appears to occur before carburization, leading to a compact Fe metal crystalline structure within which carbon atoms required to form the carbide diffuse very slowly. Temperatureprogrammed reduction of the samples in H_2 indicates that the addition of Zn appears not to influence the reduction of Fe oxides. While K inhibits the reduction of Fe oxides in H_2, Cu decreases the reduction temperature because hydrogen dissociates on Cu surface atoms and migrates as H-atoms to Fe oxide crystallites that are in contact with it as CuO is reduced at low temperatures.

A mathematical model is being developed for the H_2 and CO isotopic transient studies of the density and interaction dynamics of active sites in catalysts. Initial efforts have focused on the development of parameter estimation methods to calculate rate constants and capacities for multi-compartment models of FTS catalyst surfaces.

Fischer-Tropsch synthesis was carried out on a catalyst (Zn/Fe = 0.07, 2 at.% K, 1 at.% Cu) at 270 ^{o}C and 5 atm. At similar conditions, the FT synthesis results were in good agreement with the literature data using a similar catalyst. This fact certifies our reactor operation, data acquisition, and data analysis procedures. The effects of CO_2 addition on the rate of water-gas shift reactions and on the CO_2 selectivity during FTS were also investigated on this catalyst. It shows that CO_2 addition decreases the net CO_2 selectivity by decreasing the net rate of water-gas shift without any significant inhibition of FTS reaction rates. CO conversion rate to hydrocarbons increased with the added CO_2 partial pressure. Although CO_2 addition can be used to decrease CO_2 yields during FT reactions, the partial pressure of CO_2 required to stop water-gas shift reactions may be too high to be of practical use.

In addition, FT synthesis reactions were carried out on one of our Fe-Zn-K-Cu catalysts (Zn/Fe = 0.1, promoted with 2 at.% K and 1 at.% Cu) at different temperatures and pressures (220 ^{o}C, 31.6 atm; 235 ^{o}C, 21.4 atm; 270 ^{o}C, 5 atm). The reaction results were compared at similar CO conversion for all three FT synthesis reaction conditions.

It was found that the methane selectivity was very high (>10 %) and the C_{13+} hydrocarbon selectivity was very low (~ 14 %) at the high temperature and low pressure (270 ^{o}C, 5 atm). In contrast, the methane selectivity was very low (~3 %) and the C_{13+} hydrocarbon selectivity was very high (>50%) at lower temperatures and higher pressure (220 ^{o}C, 31.6 atm; 235 ^{o}C, 21.4 atm). These facts suggest that the low temperatures and high pressures favor the formation of higher molecular weight hydrocarbons and high temperature and low pressure favor the formation of lower molecular weight hydrocarbons. CO_2 selectivity increased as the reaction temperature increased, suggesting that the rate of water-gas shift reaction increases with temperature, and water-gas shift reaction does not reach thermodynamic equilibrium during FT synthesis reaction since water-gas shift is an exothermic reaction. This is why the addition of CO_2 did not significantly decrease the CO_2 selectivity. The olefin content also increased as the reaction temperature increased. It appears that the low temperatures and high pressures increase the probability of olefin readsorption and chain growth, which concurrently leads to their desorption as paraffins and to a lower olefin selectivity. Reaction rates on this Fe-Zn-K-Cu catalyst are similar to those obtained on the Co-based catalyst (12 wt.% Co/SiO_2) at lower temperatures.

CAER

Copper is a promoter for the FT synthesis. The FT rate increased with increasing copper loading in the range reported here (0 to 2 atomic ratio per 100 Fe). The effect of copper on FT kinetics has been studied. According to a proposed kinetic expression, the FT reaction rate is dependent on a rate constant, k and an adsorption parameter, b. Copper has been found to increase the rate constant and decrease the adsorption parameter, both of which cause an increase in the Fischer-Tropsch rate.

Copper also increased the water gas shift rate; however, it did not increase CO_2 selectivity when comparisons were made at similar conversion. The water gas shift reaction quotient only approaches the equilibrium constant at high conversion; furthermore, copper did not increase the reaction quotient.

The effect of copper on product selectivity has been determined over a wide range of conversions. Accurate comparisons of catalyst selectivity must be made at similar syngas conversion because selectivity can be greatly affected by the conversion. For example, methane selectivity increased and alkene selectivity decreased with increasing conversion. Copper had a similar effect on product selectivity as potassium. Methane selectivity decreased and products heavier than C_{11} increased with increasing copper loading. Copper did not effect alkene selectivity or the isomerization of 1-alkenes to 2-alkenes.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high-α catalysts.

No scheduled or further activity to report.

Task 2. Catalyst Testing

The objective of this task is to obtain catalyst performance on the catalysts prepared in Task 1.

Impact of Copper on an Alkali Promoted Iron Fischer-Tropsch Catalyst

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Introduction

Copper has traditionally been added to precipitated iron Fischer-Tropsch (FT) catalysts to facilitate reduction of Fe_2O_3 to zero valent iron during activation (1) by lowering the reduction temperature when activating with hydrogen, carbon monoxide or syngas (2). This is particularly important when activating with hydrogen because metallic iron which is formed will sinter easily if the temperature is too high; however, it is not as critical when activating with carbon monoxide or syngas because iron carbides are formed and they are not as susceptible to sintering.

The effect of copper on activity and selectivity has not been studied as thoroughly as its effect on catalyst activation. Kölbel reported that copper loadings less than 0.1 % (weight % relative to iron) were sufficient to produce an active catalyst and that increased copper loading had no effect on FT activity (3). It has previously been shown that copper increases the activity of precipitated iron catalysts when operating at low temperature (<250^{O}C) (2). Bukur et al. have reported that copper increases FT activity and water gas shift activity (4). In addition, they reported that copper increased the average molecular weight of the product and increased hydrogenation of alkenes and isomerization of 1-alkenes. Soled et al. have reported that promotion with copper in conjunction with potassium increased FT activity but had little effect on alkene selectivity (5).

Water gas shift activity and FT selectivity have been shown to depend on syngas conversion (6). To determine the true impact of copper on FT selectivity and water gas shift activity, comparisons should be done at similar conversion. No such study has been reported for the effects of copper. Herein are reported the effects of copper on FT activity and selectivity and water gas shift activity over a wide range of syngas conversions.

Experimental

A base catalyst with atomic composition 100Fe/4.6Si was prepared by precipitation as previously reported (7). The catalyst was impregnated with aqueous K_2CO_3 to give an atomic composition of 100Fe/4.6Si/1.4K. Copper was added by impregnation with aqueous $Cu(NO_3)_2 \cdot 3H_2O$. Catalyst compositions in atomic ratios were:

100Fe/4.6Si/1.4K
100Fe/4.6Si/0.10Cu/1.4K
100Fe/4.6Si/2.0Cu/1.4K

Approximately 5 g of catalyst were mixed with 300 g of Ethylflo 164 decene trimer in a one liter stirred tank reactor. Catalysts were activated with carbon monoxide at 270^{O}C and 1.3 MPa for 24 hours. Following activation, temperature and pressure were maintained and syngas (H_2/CO=0.67) was started at a space velocity of 10 l (STP) h^{-1} g-Fe^{-1}. The reactor stirring speed was maintained at 750 rpm. Within eight days syngas conversion had stabilized and the space velocity was varied between 5 and 65 l (STP) h^{-1} g-Fe^{-1}. Each space velocity was maintained for approximately 24 hours after which liquid samples were taken and a material balance was calculated. The space velocity was returned to 10 l (STP) h^{-1} g-Fe^{-1} after about two weeks on line to check for deactivation.

Results

FT Activity

Syngas conversion for each catalyst as a function of the reciprocal space velocity is shown in Figure 1. Copper increased syngas conversion over the entire range of space velocities studied. Copper also increased hydrocarbon productivity (Figure 2). At the lowest space velocity the hydrocarbon productivity was about the same for all three catalysts (~1.1 g h^{-1} g-Fe^{-1}). As the space velocity was increased, hydrocarbon productivity increased with increasing copper loading. At the highest space velocity, the hydrocarbon productivity was 5.3, 3.9 and 3.0 g h^{-1} g-Fe^{-1} for the 100Fe/4.6Si/2.0Cu/1.4K, 100Fe/4.6Si/0.10Cu/1.4K and 100Fe/4.6Si/1.4K catalysts, respectively.

Water gas shift Activity

The rate of the water gas shift reaction is defined as the rate of carbon dioxide formation, mol h^{-1}g-Fe^{-1}, in this study. In general, the water gas shift rate increased initially with increasing space velocity. The water gas shift rate for the 100Fe/4.6Si/2.0Cu/1.4K catalyst increased over the entire range of space velocities studied; however, it leveled off for the 100Fe/4.6Si/0.10Cu/1.4K catalyst and reached a maximum for the 100Fe/4.6Si/1.4K catalyst (Figure 3). Copper slightly increased the water gas shift rate at the lowest space velocity. As the space velocity increased the impact of copper became more pronounced. At the highest space velocity, the water gas shift rates were 0.21, 0.14 and 0.1 for the 100Fe/4.6Si/2.0Cu/1.4K, 100Fe/4.6Si/0.10Cu/1.4K and 100Fe/4.6Si/1.4K catalysts, respectively. Similarly copper increased the water gas shift rate at all conversion levels studied, although the water gas shift rates were converging at the highest conversion (Figure 4). The approach to equilibrium for the water gas shift can be measured by the reaction quotient:

$$RQ_{WGS} = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}. \tag{1}$$

The reaction quotient increased with increasing conversion; however, only at syngas conversion greater than 90% did the water gas shift reaction approach equilibrium (Figure 5). Copper had no effect on the water gas shift reaction quotient when compared at similar conversion.

FT Rate Versus Water Gas Shift Rate

The rate of the water gas shift and FT reactions can be defined by equations 2 and 3:

$$r_{wgs} = r_{CO_2} \tag{2}$$

$$r_{FT} = r_{CO} - r_{CO_2} \tag{3}$$

where r_{CO_2} is the rate of CO_2 formation and r_{CO} is the rate of CO conversion. The FT rate dominated the water gas shift rate at the highest space velocities (Figure 6). The FT and water gas shift rates decreased as the space velocity decreased and conversion increased. As the space velocity decreased the water gas shift rate approached the FT rate.

Selectivity

Carbon monoxide efficiency was not effected by copper promotion. In general, the selectivity to carbon dioxide decreased with decreasing syngas conversion (Figure 7). Copper had little effect on alkene selectivity (Figure 8) or isomerization of 1-butene (Figure 9) over the entire range of conversions studied. Methane selectivity was fairly constant up to 50-60 % conversion; however, at higher conversions, methane selectivity increased with increasing conversion. In general, the hydrocarbon selectivity shifted to heavier products with decreasing conversion (Figure 11). Copper lowered the methane selectivity at all conversions (Figure 10) and increased C_{12} and heavier products (Figure 11).

Kinetics

Satterfield et al. have proposed the following kinetic expression for the rate of consumption of syngas by the FT synthesis:

$$-r_{CO+H_2} = \frac{kP_{CO}P^{2}_{H_2}}{P_{CO}P_{H_2} + bP_{H_2O}} \qquad (4)$$

where k is the intrinsic rate constant, b is the product of the adsorption equilibrium constant of CO and the desorption equilibrium constant of H_2O and the remaining variables are the partial pressures of CO, H_2 and H_2O (8). Equation 4 can be rearranged to give the following linear equation:

$$\frac{P_{H_2}}{-r_{CO+H_2}} = \frac{1}{k} + \frac{b}{k}\frac{P_{H_2O}}{P_{CO}P_{H_2}}. \qquad (5)$$

A plot of $P_{H_2}/-r_{CO+H_2}$ versus $P_{H_2O}/(P_{CO}P_{H_2})$ will give a straight line with slope equal to b/k and y-intercept equal to 1/k if data fit the model. Data for the three runs are presented in this manner in Figure 12 and results are listed in Table 1. The rate constant, k increased with increasing copper and the adsorption parameter, b decreased with increasing copper.

Discussion

Activity and selectivity data for each catalyst are listed in Tables 2 through 4. Conversion and hydrocarbon productivity increased with increasing copper loading over the range of copper loadings studied and hydrocarbon productivity increased by a factor of 3 to 5 upon increasing the space velocity (decreasing conversion) from 5 to 65 l (STP) h^{-1} g-Fe^{-1}. The kinetic expression proposed by Satterfield et al. (8) adequately described the data acquired for all three catalysts. Copper increased the intrinsic FT rate constant and also decreased the adsorption parameter, b. Examination of equation 4 reveals that both of these effects result in an increase in the FT rate. The effect of copper on the FT rate is somewhat different than the effect of potassium. Potassium was previously found to decrease the intrinsic rate constant, k and the adsorption parameter, b (9). Since these trends have an opposite effect on FT rate (equation 4), the effect of potassium depended on the conversion. At high conversion, increasing potassium slightly increased activity, at intermediate conversion (50%) there was an optimum potassium loading and at low conversion increasing potassium decreased FT activity.

Water gas shift

It is conventional wisdom that copper increases carbon dioxide selectivity and the water gas shift reaction quotient (4). In the present study it was found that copper increased the water gas shift rate; however, it did not effect the carbon dioxide selectivity or the water gas shift reaction quotient when comparisons were made at the same syngas conversion. The FT reaction rate was always higher than the water gas shift reaction. This can be seen in Figure 6 where the ratio of the water gas shift rate to the FT rate for all three catalysts increased from about 0.4 at the highest space velocity to greater than 0.8 at the lowest space velocity. The rate of the water gas shift reaction cannot be greater than the rate of the FT reaction because the water gas shift reaction is limited by the rate of water produced by the FT reaction.

FT reaction $$CO + (1+(n/2))H_2 \rightarrow CH_n + H_2O \tag{6}$$

water gas shift $$CO + H_2O \rightarrow CO_2 + H_2 \tag{7}$$

It has been reported that copper effects hydrocarbon selectivity in much the same way as potassium, except secondary reactions are slightly enhanced (alkene hydrogenation and 1-alkene isomerization) (4); however, comparisons were not made at similar conversions. In the present study, methane selectivity was constant up to a conversion of approximately 50%, irrespective of copper loading. Above 50% conversion, methane selectivity increased with increasing conversion. Increasing copper did significantly lower methane selectivity and increase the selectivity to heavy products. Alkene selectivity and isomerization of 1-alkenes was not effected by copper when comparisons were made at similar conversion.

Conclusions

Copper is a promoter for the FT synthesis. The FT rate increased with increasing copper loading in the range reported here (0 to 2 atomic ratio per 100 Fe). The effect of copper on FT kinetics has been studied. According to a proposed kinetic expression, the FT reaction rate is dependent on a rate constant, k and an adsorption parameter, b. Copper has been found to increase the rate constant and decrease the adsorption parameter, both of which cause an increase in FT rate.

Copper also increased the water gas shift rate; however, it did not increase CO_2 selectivity when comparisons were made at similar conversion. The water gas shift reaction quotient only approaches the equilibrium constant at high conversion; furthermore, copper did not increase the reaction quotient.

The effect of copper on product selectivity has been determined over a wide range of conversions. Accurate comparisons of catalyst selectivity must be made at similar syngas conversion because selectivity can be greatly affected by the conversion. For example, methane selectivity increased and alkene selectivity decreased with increasing conversion. Copper had a similar effect on product selectivity as potassium. Methane selectivity decreased and products heavier than C_{11} increased with increasing copper loading. Copper did not effect alkene selectivity or the isomerization of 1-alkenes to 2-alkenes.

References

1. M. E. Dry, in J. R. Anderson and M. Boudart (Editors), Catalysis Science and Technology, Vol. 1, Springer-Verlag, New York, 1981, p. 179.
2. R. J. O'Brien, L. Xu, R. L. Spicer, S. Bao, D. R. Milburn, B. H. Davis, *Catal. Today*, 36 (1997) 325.
3. H. Kölbel, M. Ralek, *Catal. Rev. Sci. Eng.*, 21 (1980) 225.
4. D. B. Bukur, D. Mukesh, S. A. Patel, *Ind. Eng. Chem. Res.*, 29 (1990) 194.
5. S. L. Soled, E. Iglesia, S. Miseo, B. A. DeRites, R. A. Fiato, *Topics in Catal.*, 2 (1995) 193.
6. Raje, A. P., Davis, B. H., *Catal. Today* **36**, 335 (1997).
7. R. J. O'Brien, L. Xu, R. L. Spicer, B. H. Davis, *Energy & Fuels*, 10 (1996) 921.
8. G. A. Huff Jr., C. N. Satterfield, *Ind Eng. Chem. Process Des. Dev.*, 23 (1984) 696.
9. A. P. Raje, R. J. O'Brien, B. H. Davis, *J. Catalysis*, 180 (1998) 36.

Table 1

Effect of Copper on Kinetic Parameters

	k (mol h^{-1}g-$Fe^{-1}$$kPa^{-1}$)	b
100Fe/4.6Si/1.4K	1.75×10^{-3}	3040
100Fe/4.6Si/0.1Cu/1.4K	2.04×10^{-3}	1940
100Fe/4.6Si/2.0Cu/1.4K	2.93×10^{-3}	1590

Table 2

Activity and Selectivity for 100Fe/4.6Si/1.4K Catalyst

	Space Velocity (sl h^{-1}g-Fe^{-1})								
	5.0	**6.67**	**10**	**15**	**22**	**30**	**40**	**50**	**65**
$CO + H_2$ Conversion %	80	76	71	57	44	36	29	25	20
Hydrocarbon Productivity (g h^{-1}g-Fe^{-1})	0.89	1.08	1.53	1.91	2.12	2.41	2.73	2.89	3.03
Water-Gas Shift									
$P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	20	15	9.7	4.0	2.4	1.6	1.2	1.0	0.92
H_2/CO usage ratio	0.57	0.58	0.60	0.65	0.72	0.78	0.81	0.90	0.96
Selectivity C basis									
CO_2	46	47	46	44	42	38	34	32	30
CH_4	7.1	7.1	4.8	5.3	5.2	5.0	4.8	4.7	4.9
Selectivity (wt.%)									
CH_4	7.9	7.9	6.5	5.9	5.8	5.6	5.4	5.2	5.5
C_2-C_4	27	27	24	23	24	23	22	22	22
C_5-C_{11}	35	36	34	35	34	32	32	30	30
C_{12}+	31	29	36	36	37	39	41	43	43
alkene									
C_2-C_4	60	63	71	77	80	82	83	85	85
C_5-C_{11}	69	73	75	78	82	83	84	85	75

Table 3

Activity and Selectivity for 100Fe/4.6Si/0.10Cu/1.4K Catalyst

	Space Velocity (sl h^{-1}g-Fe^{-1})								
	5.0	**6.67**	**10**	**15**	**22**	**30**	**40**	**50**	**65**
CO + H_2 Conversion %	86	83	76	64	54	44	37	31	25
Hydrocarbon Productivity (g h^{-1}g-Fe^{-1})	0.87	1.15	1.64	2.15	2.75	3.00	3.50	3.87	3.89
Water-Gas Shift									
$P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	48	32	12	6.3	3.6	2.4	1.8	1.5	1.3
H_2/CO usage ratio	0.57	0.58	0.60	0.60	0.64	0.68	0.72	0.71	0.78
Selectivity C basis									
CO_2	51	49	46	44	41	41	37	34	34
CH_4	8.7	7.9	6.0	5.2	4.7	5.1	4.8	4.9	5.3
Selectivity (wt.%)									
CH_4	9.7	8.9	6.7	5.9	5.3	5.7	5.4	5.4	6.0
C_2-C_4	29	28	23	22	20	22	21	20	22
C_5-C_{11}	42	39	35	34	31	33	33	31	32
C_{12}+	19	24	35	38	44	39	40	44	40
alkene									
C_2-C_4	57	58	69	75	79	81	83	83	85
C_5-C_{11}	66	67	73	77	80	82	82	84	84

Table 4

Activity and Selectivity for 100Fe/4.6Si/2.0Cu/1.4K Catalyst

	Space Velocity (sl h^{-1}g-Fe^{-1})								
	5.0	**6.67**	**10**	**15**	**22**	**30**	**40**	**50**	**65**
CO + H_2 Conversion %	89	88	86	77	66	56	48	42	35
Hydrocarbon Productivity (g h^{-1}g-Fe^{-1})	1.02	1.24	1.92	2.51	3.20	3.74	4.49	4.62	5.30
Water-Gas Shift									
$P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	42	56	30	14	6.5	4.3	2.6	2.0	1.6
H_2/CO usage ratio	0.58	0.60	0.58	0.60	0.63	0.66	0.66	0.75	0.74
Selectivity C basis									
CO_2	44	47	45	46	44	43	40	40	37
CH_4									
Selectivity (wt.%)									
CH_4	7.3	7.9	7.0	6.2	5.5	5.3	4.9	5.4	5.2
C_2-C_4	22	24	21	21	20	20	18	20	19
C_5-C_{11}	32	27	29	33	32	30	27	31	30
C_{12}+	39	41	42	40	42	45	49	44	46
alkene									
C_2-C_4	58	57	60	69	75	79	81	82	83
C_5-C_{11}	65	67	67	70	75	79	81	82	83

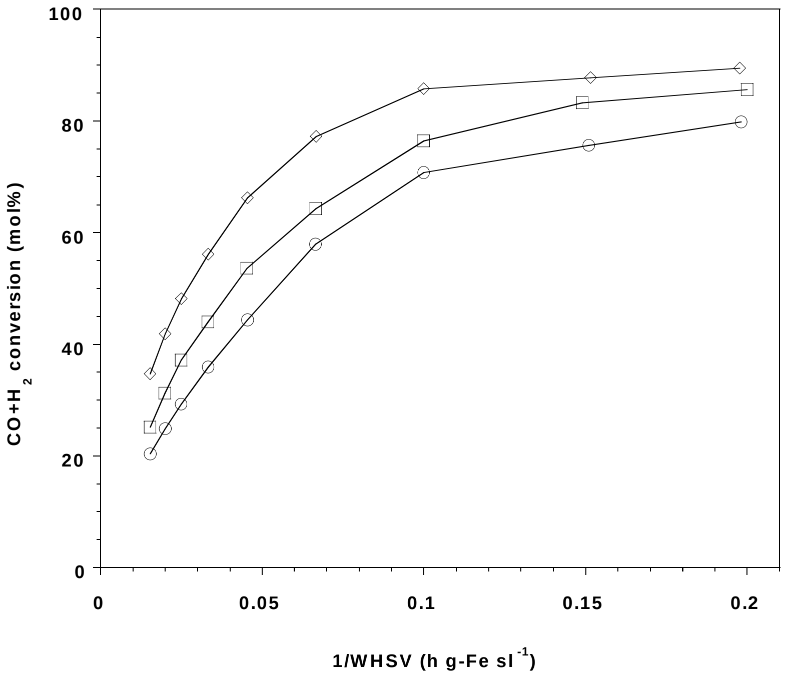

Figure 1. Syngas conversion as a function of reciprocal space velocity. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

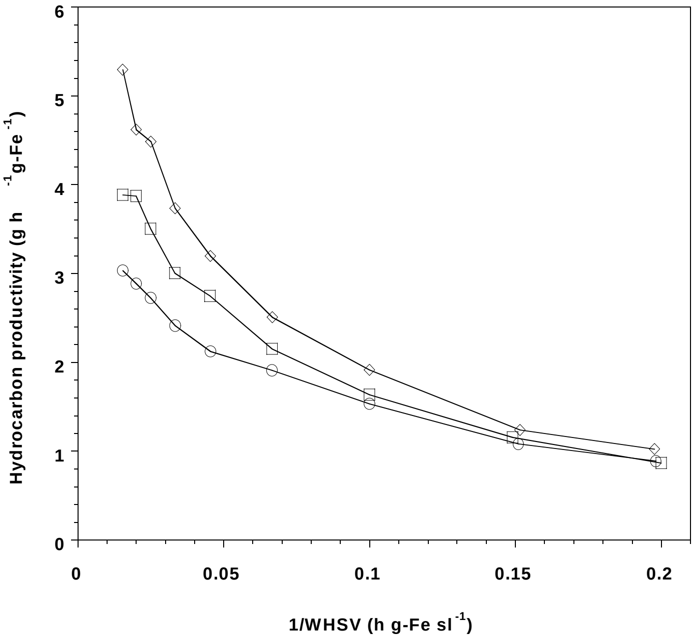

Figure 2. Hydrocarbon productivity as a function of reciprocal space velocity. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

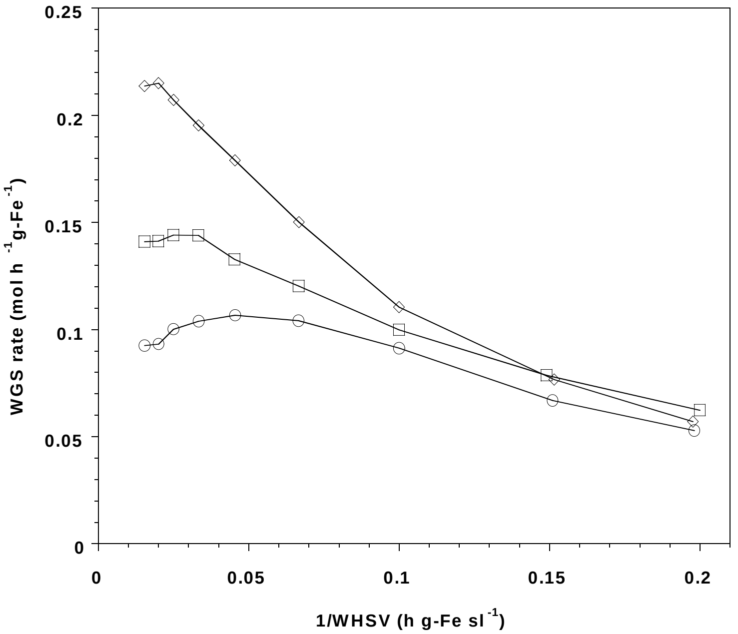

Figure 3. Water gas shift rate as a function of reciprocal space velocity. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

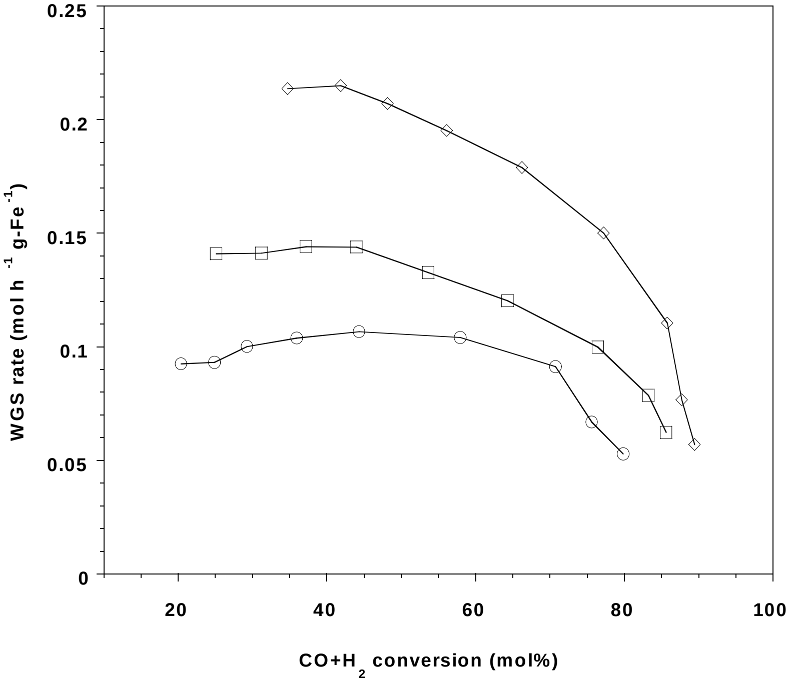

Figure 4. Water gas shift rate as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

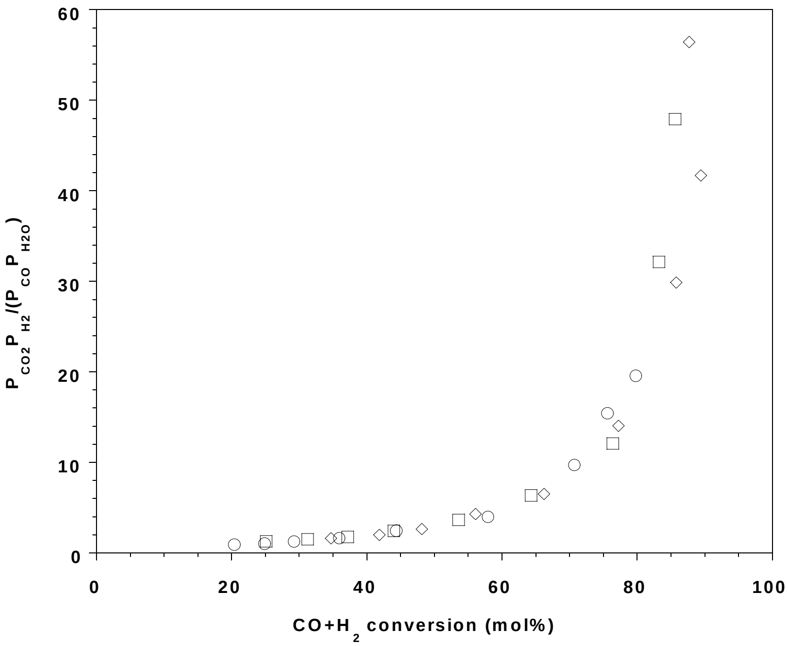

Figure 5. Water gas shift reaction quotient as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

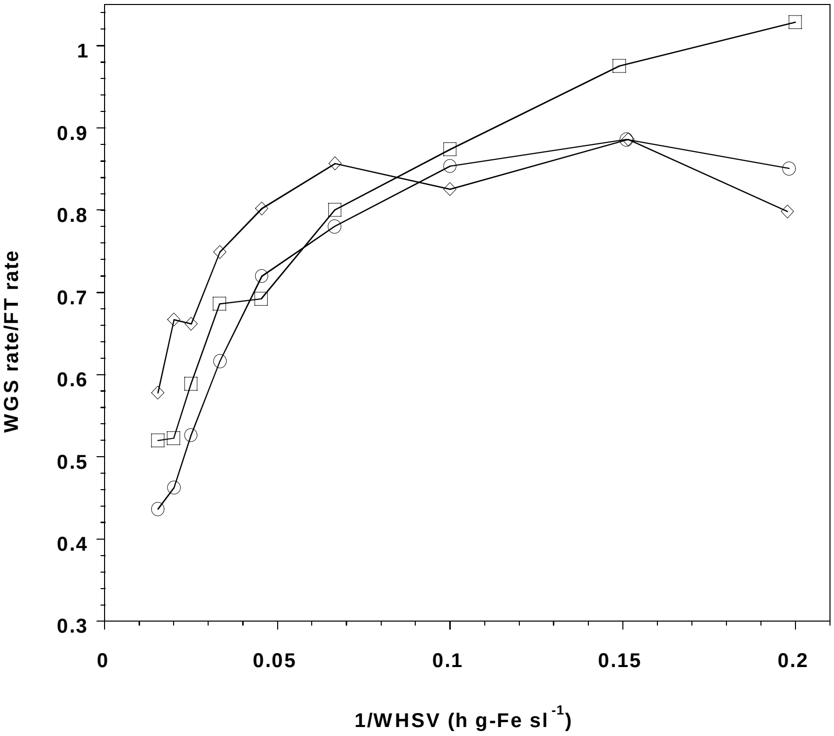

Figure 6. Ratio of water gas shift rate to FT rate as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

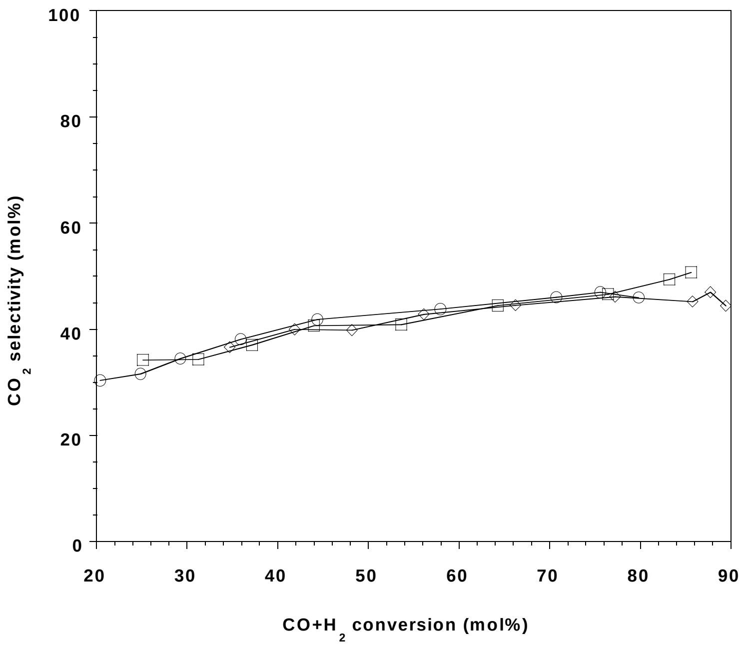

Figure 7. Carbon dioxide selectivity as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

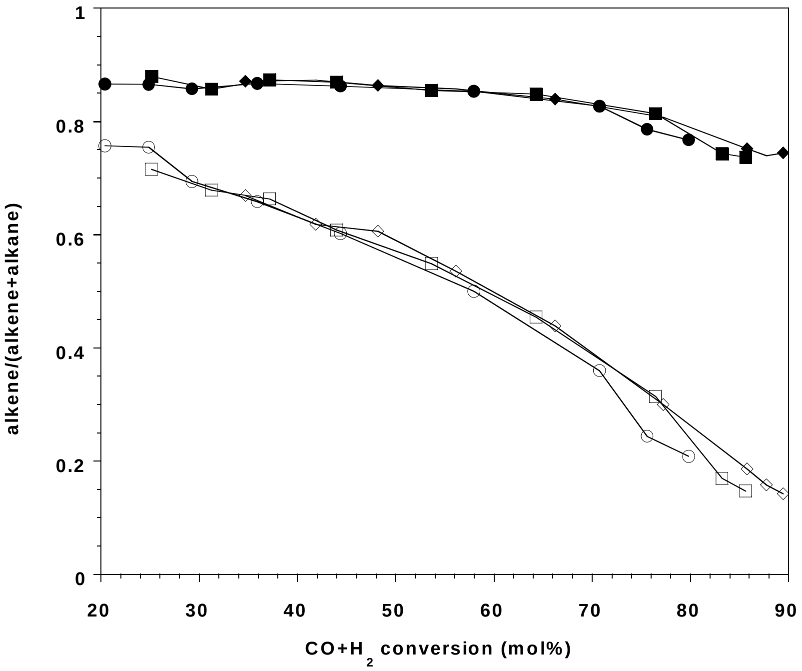

Figure 8. Alkene selectivity of C_2 (open symbols) and C_4 (closed symbols) as a function of syngas conversion. ○ and ●, 0 Cu, □ and ■, 0.1 Cu, ◊ and ◆, 2.0 Cu.

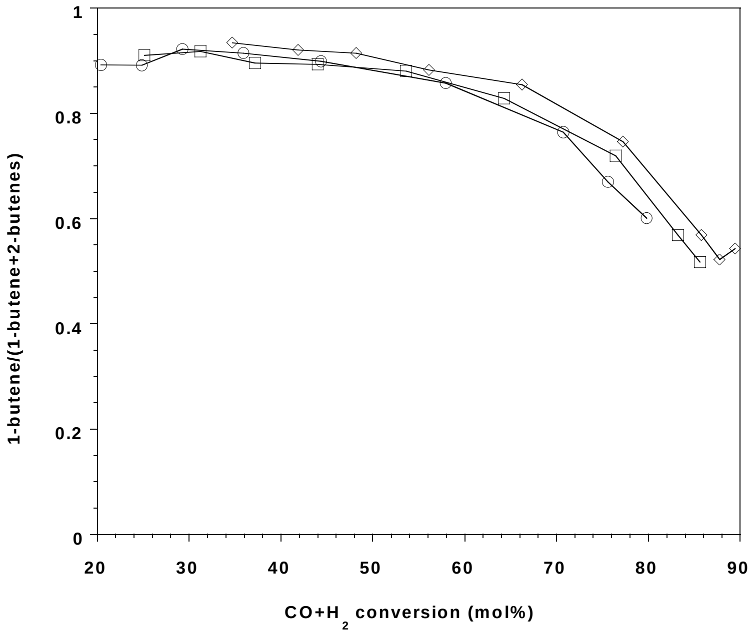

Figure 9. 1-butene selectivity as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

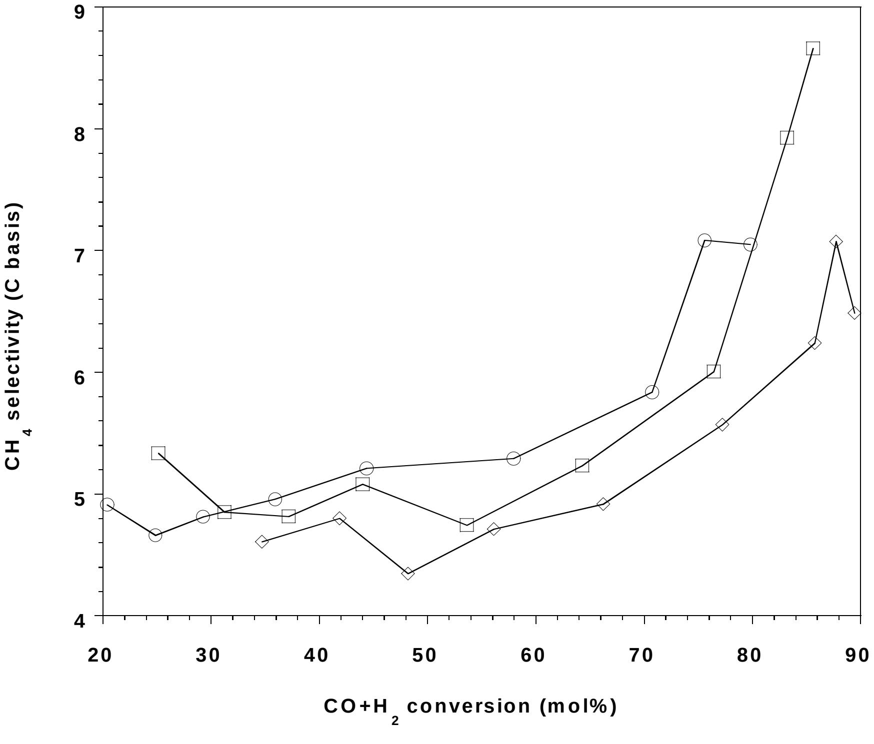

Figure 10. Methane selectivity as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

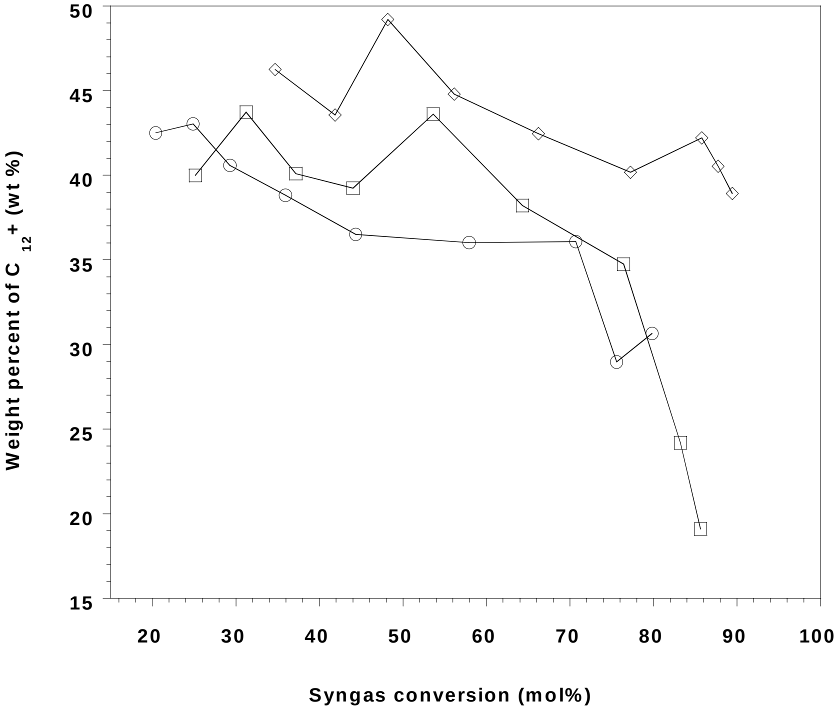

Figure 11. Selectivity of C_{12} and heavier products as a function of syngas conversion. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

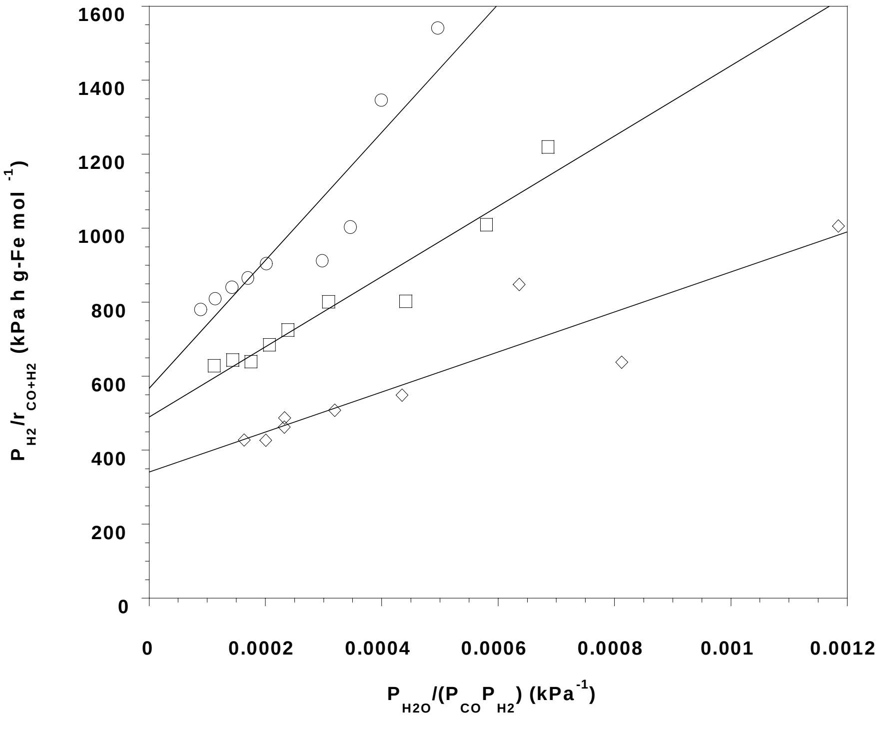

Figure 12. FT rate data fit according to equation 5. ○, 0 Cu, □, 0.1 Cu, ◊, 2.0 Cu.

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

No scheduled or further activity to report.

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

No scheduled or further activity to report.

Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalsyts.

No scheduled or further activity to report.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

This task is approximately 90% complete. Due to the size of the document, it has been submitted as a separate report to the AAD Document Control labeled Task 6.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled or further activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

No scheduled or further activity to report.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled for further activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled or further activity to report.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H_2 on multi-component catalysts based on Fe as the active component.