Catalysis Letters Vol. 94, Nos. 1–2, April 2004 (© 2004)

Impact of copper on an alkali promoted iron Fischer–Tropsch catalyst

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Received 14 November 2003; accepted 2 February 2004

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 [M.E. Dry, in: J.R. Anderson and M. Boudart (eds), *Catalysis Science and Technology*, Vol. 1 (Springer-Verlag, New York, 1981) p. 179] by lowering the reduction temperature when activating with hydrogen, carbon monoxide or syngas [R.J. O'Brien *et al.*, Catal. Today 36 (1997) 325]. 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 [H. Kölbel and M. Ralek, Catal. Rev. Sci. Eng. 21 (1980) 225]. It has previously been shown that copper increases the activity of precipitated iron catalysts when operating at low temperature (< 250 °C) [2]. Bukur and Mukesh have reported that copper increases FT activity and water gas shift activity [D.B. Bukur *et al.*, Ind. Eng. Chem. Res. 29 (1990) 194]. 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 [S.L. Soled *et al.*, Top. Catal. 2 (1995) 193]. Water gas shift activity and FT selectivity have been shown to depend on syngas conversion [A.P. Raje and B.H. Davis, Catal. Today 36 (1997) 335]. 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.

KEY WORDS: copper; alkali promoted iron FT catalyst; effect of copper on selectivity; effect of copper on activity.

1. Experimental

A base catalyst with atomic composition 100Fe/4.6Si was prepared by precipitation as previously reported [1]. The catalyst was calcined at 350 °C for 4 h prior to impregnation. 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 $Cu(NO_3)_2 3H_2O$. Catalyst compositions in atomic ratio 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 1 L stirred tank reactor. Catalysts were activated with carbon monoxide at 270 °C and 1.3 MPa for 24 h. Following activation, temperature and pressure were maintained and syngas ($H_2/CO = 0.67$) was started at a space velocity of 10 NL (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 NL (STP) h^{-1} g-Fe^{-1}. Each space velocity was maintained for approximately 24 h after which liquid samples were taken and a material balance was calculated. The space velocity was returned to 10 NL (STP) h^{-1} g-Fe^{-1} after about 2 weeks on line and at intervals thereafter to check for any catalyst deactivation.

2. Results

2.1. *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 utilized, 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.

2.2. *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 decreased initially with increasing space velocity. The water gas

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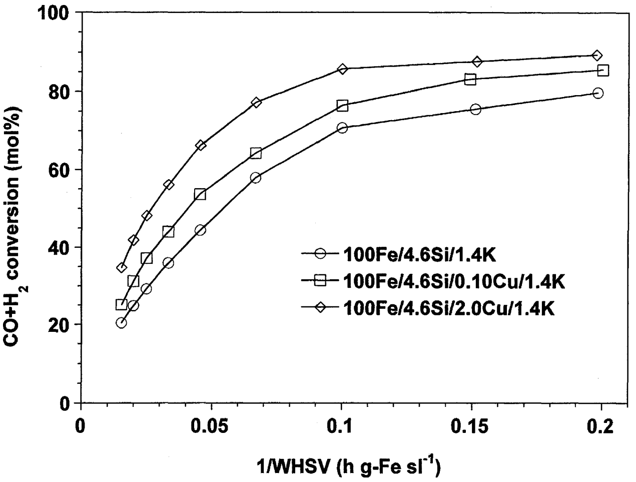

Figure 1. Syngas conversion as a function of reciprocal space velocity (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

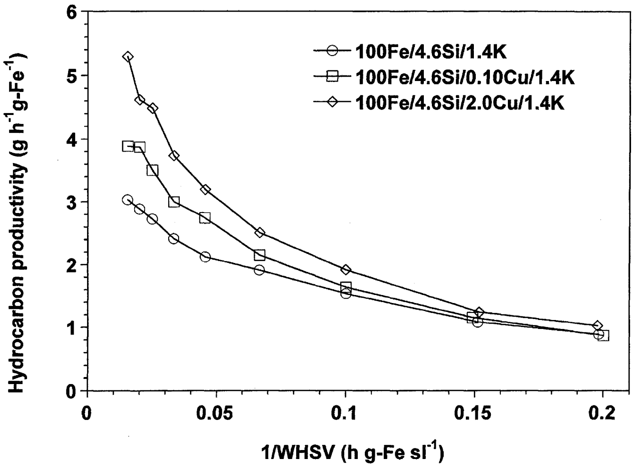

Figure 2. Hydrocarbon productivity as a function of reciprocal space velocity (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

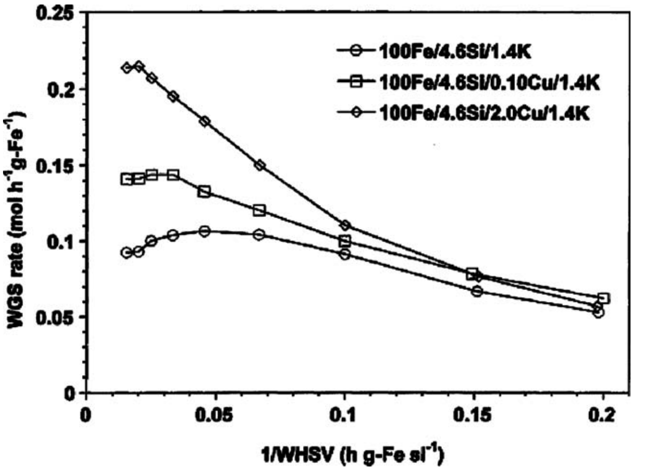

Figure 3. Water–gas shift rate as a function of reciprocal space velocity (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

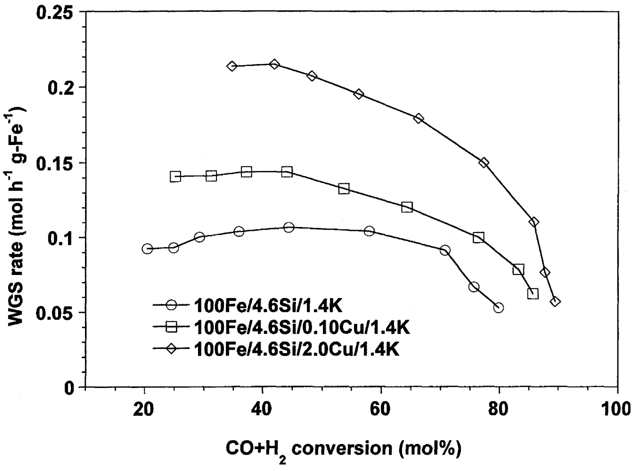

Figure 4. Water–gas shift rate as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

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:

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

The reaction quotient increased with increasing conversion; however, only at syngas conversion greater than 90% did the water gas shift reaction approach the equilibrium value ($\mathrm{RQ_{WGS}} = 62$) (figure 5). Copper had no effect on the water gas shift reaction quotient when compared at similar conversion.

2.3. *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:

$$r_{\mathrm{WGS}} = r_{\mathrm{CO_2}} \tag{2}$$

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

where $r_{\mathrm{CO_2}}$ 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

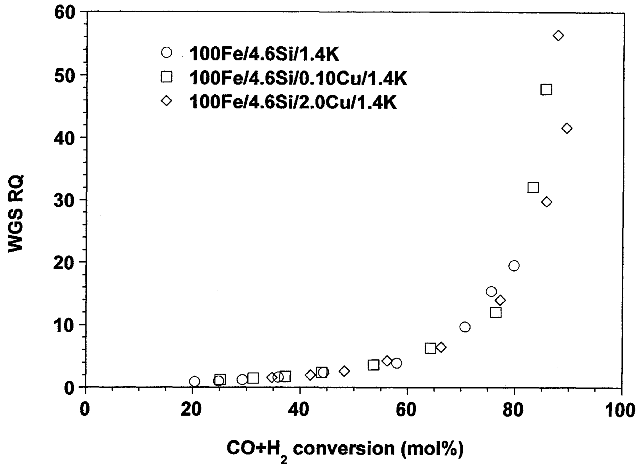

Figure 5. Water–gas shift reaction quotient as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

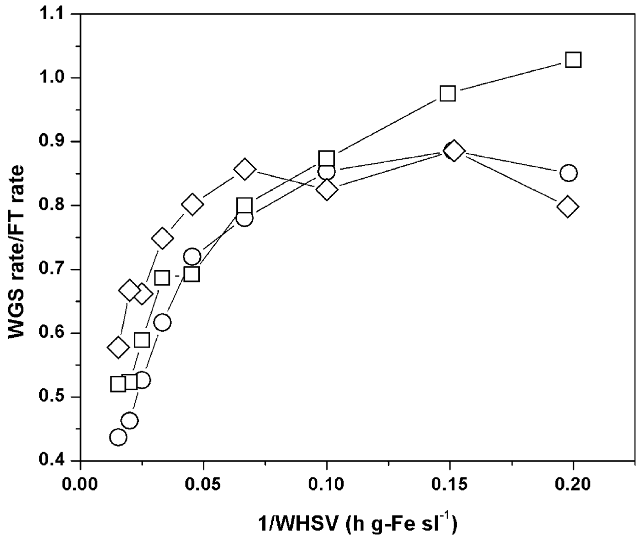

Figure 6. Ratio of water–gas shift rate to FT rate as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

space velocity decreased the water gas shift rate approached the FT rate.

2.4. *Selectivity*

Carbon monoxide efficiency was not effected by copper promotion. In general, the selectivity to carbon dioxide increased with increasing 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 (figure 10). 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).

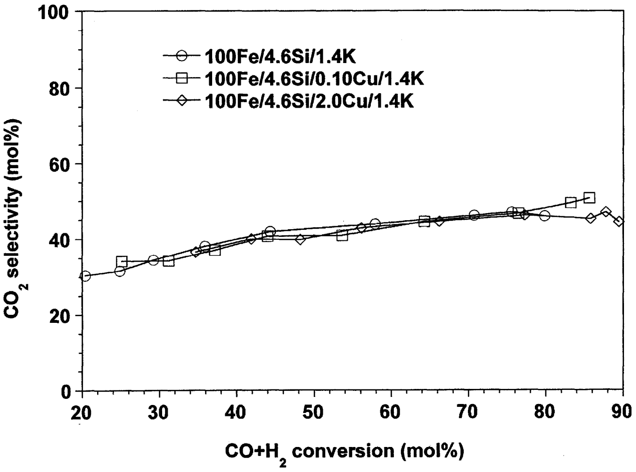

Figure 7. Carbon dioxide selectivity as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

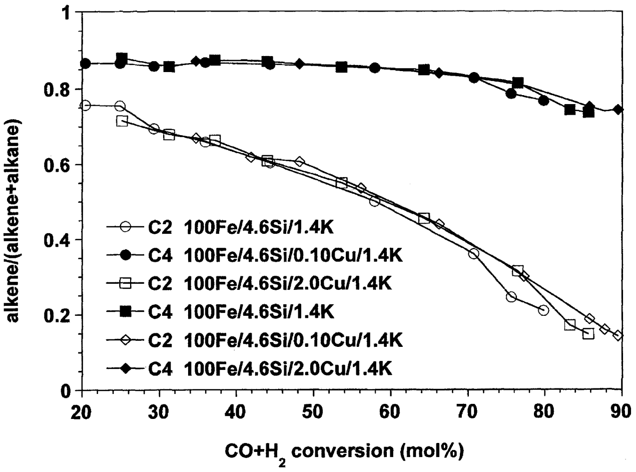

Figure 8. Alkene selectivity of C_2 (open symbols) and C_4 (closed symbols) as a function of syngas conversion (○ and ●, 0 Cu; □ and ■, 0.1 Cu; ◇ and ◆, 2.0 Cu).

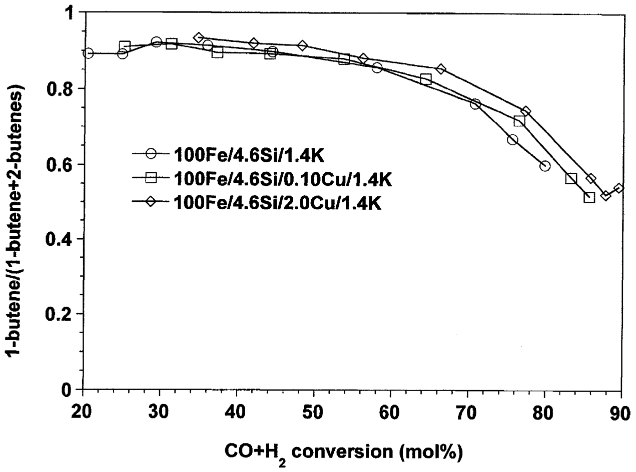

Figure 9. 1-Butene selectivity as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

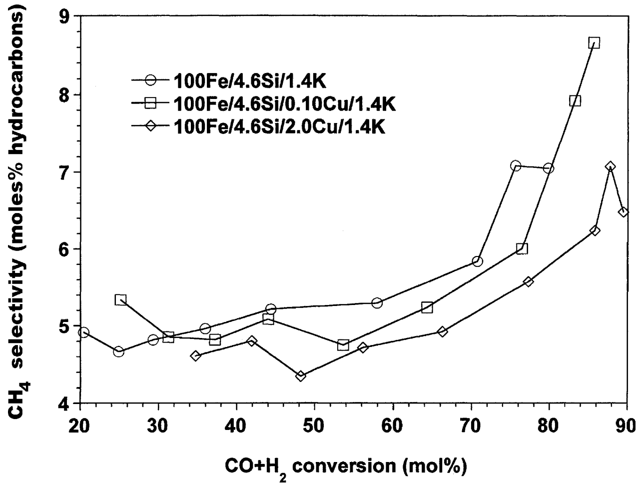

Figure 10. Methane selectivity as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

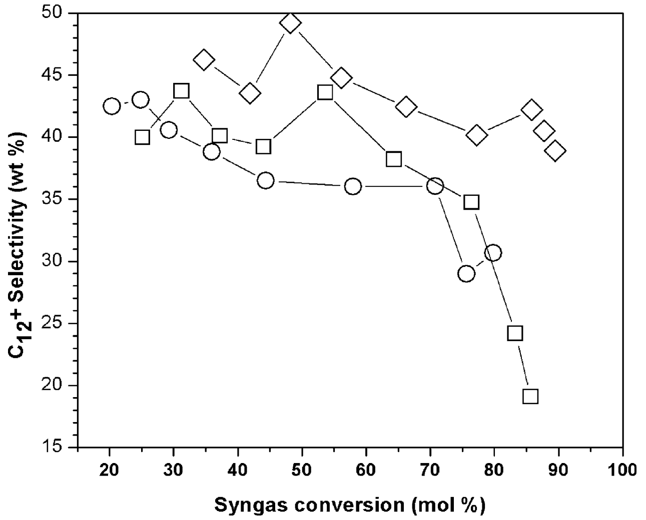

Figure 11. Selectivity of C_{12} and heavier products as a function of syngas conversion (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

2.5. *Kinetics*

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

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

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 [2]. Equation (4) can be rearranged to give the following linear equation:

$$\frac{P_{\mathrm{H_2}}}{-r_{\mathrm{CO+H_2}}} = \frac{1}{k} + \frac{bP_{\mathrm{H_2O}}}{kP_{\mathrm{CO}}P_{\mathrm{H_2}}} \qquad (5)$$

A plot of $P_{\mathrm{H_2}}/-r_{\mathrm{CO+H_2}}$ versus $P_{\mathrm{H_2O}}/(P_{\mathrm{CO}}P_{\mathrm{H_2}})$ 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.

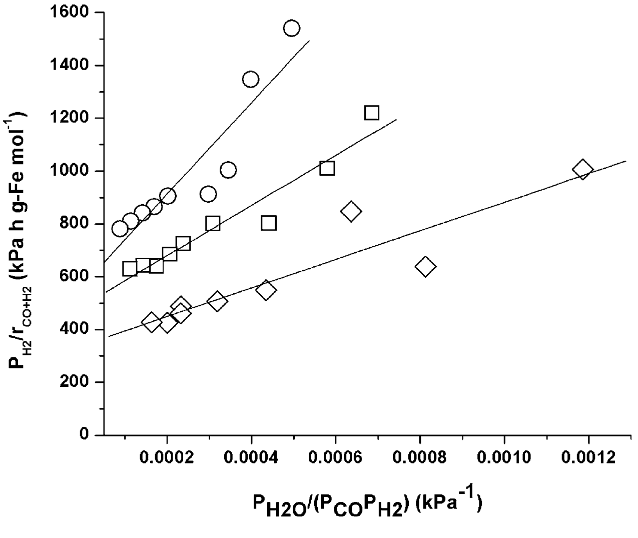

Figure 12. FT rate data fit according to equation 5 (○, 0 Cu; □, 0.1 Cu; ◇, 2.0 Cu).

Table 1
Effect of copper on kinetic parameters

	k (mol h^{-1} g-Fe^{-1} kPa^{-1})	b
100Fe/4.6Si/1.4K	1.76×10^{-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

3. Discussion

Activity and selectivity data for each catalyst are listed in tables 2–4. Conversion and hydrocarbon productivity increased with increasing copper loading over the range of copper loadings studied and hydrocarbon productivity increased by a factor of 3–5 upon increasing the space velocity (decreasing conversion) from 5 to 65 l (STP) h^{-1} g-Fe^{-1}. The kinetic expression proposed by Huff and Satterfield [2] adequately described the data acquired for all three catalyst. 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 [3]. Since these trends have an opposite effect on FT rate (equation 4), the effect of potassium depended

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[a]	46	47	46	44	42	38	34	32	30
CH_4[b]	7.1	7.1	5.8	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

[a] Selectivity CO_2 = moles CO_2 produced/moles CO converted.
[b] Selectivity CH_4 = moles CH_4 formed/moles CO converted to hydrocarbons.

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[a]	51	49	46	44	41	41	37	34	34
CH_4[b]	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

[a] Selectivity CO_2 = moles CO_2 produced/moles CO converted.
[b] Selectivity CH_4 = moles CH_4 formed/moles CO converted to hydrocarbons.

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.

3.1. *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.

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[a]	44	47	45	46	44	43	40	40	37
CH_4[b]	6.5	7.1	6.2	5.6	4.9	4.7	4.3	4.8	4.6
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	40	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

[a] Selectivity CO_2 = moles CO_2 produced/moles CO converted.
[b] Selectivity CH_4 = moles CH_4 formed/moles CO converted to hydrocarbons.

$$\text{FT reaction} \quad CO + (1 + (n/2))H_2 \quad CH_n + H_2O \qquad (6)$$

$$\text{water gas shift } CO + H_2O \quad CO_2 + H_2 \qquad (7)$$

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 conversion. 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.

4. Conclusions

Copper is a promoter for the FT synthesis. The FT rate increased with increasing copper loading in the range reported here (0–2 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.

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