3.1.2 Effect of Potassium Promotion on Iron-Based Catalysts For Fischer-Tropsch Synthesis

ABSTRACT

The effect of potassium on catalyst activity, kinetic parameters and selectivity has been investigated for a precipitated iron catalyst that was employed with low H_2/CO ratio typical of a synthesis gas generated from coal. A wide range of synthesis gas conversions have been obtained by varying space velocities over catalysts with various potassium loadings. Differing trends in catalyst activity with potassium loading were observed depending on the space velocity or synthesis gas conversion. As potassium loading increased, the catalyst activity either decreased (low conversions), passed through a maximum (intermediate conversions) or increased (high conversions). This is shown to be a result of the increasing dependency of the Fischer-Tropsch synthesis on the hydrogen formed by the water-gas shift reaction with increasing synthesis gas conversions. Both the rate constant and the adsorption parameter in a common two-parameter Fischer-Tropsch rate expression decreased with potassium loading; therefore, observed maxima in Fischer-Tropsch rate with potassium loading can be due to the opposing influences of these parameters. The effect of potassium on alkene selectivity was dependent on the number of carbon atoms of the hydrocarbons as well as the carbon monoxide conversion level. The extent of isomerization of alkene products decreased with potassium loading, while the selectivity to methane decreased with increasing potassium content at CO conversions about 50% and higher.

INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) converts synthesis gas, a mixture of carbon monoxide and hydrogen, to hydrocarbons. The FTS reaction can be represented as:

$$CO + (1 + (n/2))\ H_2 \rightarrow CH_n + H_2O \qquad \textbf{(1)}$$

where n is the average H/C ratio of the hydrocarbons produced. Iron-based catalysts possess activity for the water gas shift (WGS) reaction. This property allows the direct processing of synthesis gas with a low H_2/CO ratio (as produced by coal gasification in advanced gasifiers) without an additional WGS reactor. The WGS reaction provides the extra hydrogen needed for the FTS.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \textbf{(2)}$$

Typical iron-based catalysts contain small amounts of potassium along with binders such as silica or alumina. The role of potassium on iron-based catalysts has been previously studied; however, the results of the effect of potassium on catalyst activity vary considerably with different researchers, different temperatures and with the presence/amount of binders used (1-4). Potassium has been shown to increase catalytic activity (1, 2, 4), decrease activity (2, 3), and in some cases the activity has been shown to reach a maximum with increasing potassium loading and then decline with further addition of potassium (1, 2). Further, systematic studies of possible reasons for catalyst activity trends have rarely been performed.

A reaction rate expression proposed (5) for the FTS is

$$-r_{CO+H_{\|}} = \frac{kP_{CO}P_{H_{\|}}^{2}}{P_{CO}P_{H_{\|}} + bP_{H_{\|}O}} \qquad \textbf{(3)}$$

Based on this rate expression, changes in catalyst FTS activity could be due to changes in: (i) rate constant, k, (ii) adsorption parameter, b, and (iii) partial pressure of water. In addition, the rate and extent of the WGS reaction has a major effect on the FTS activity, especially for a low H_2/CO ratio synthesis gas. Studies of the effect of potassium loading on the kinetic parameters of the Fischer-Tropsch Synthesis or the effect of the WGS reaction on the FTS activity have not been previously reported in detail.

Addition of potassium has been found to affect the catalyst selectivity. Potassium apparently increases the alkene content of the hydrocarbon products, increases the rate of the WGS reaction and suppresses methane formation. However, these selectivity comparisons have often been made at different synthesis gas conversion levels (3, 4). It is known that selectivity changes with synthesis gas conversion and thus a comparison at equal conversion levels would be more appropriate to discern selectivity changes (6).

In this study, a systematic comparison of the effect of increasing potassium levels on iron-based catalyst activity and selectivity is conducted. Data were obtained for each potassium level over a wide range of synthesis gas conversions by varying feed space velocities. Thus, the effect of potassium on kinetic parameters has been determined and selectivity comparisons made at equal conversion levels. An attempt is made to discern the reason(s) for changes in catalyst activity with increasing potassium levels.

EXPERIMENTAL

Catalysts

The base catalyst used was a precipitated iron-silica catalyst with atomic ratio 100Fe/4.6Si. The preparation of this catalyst using a continuous precipitation procedure has been described previously (7). Various levels of potassium were added by incipient wetness impregnation with aqueous potassium nitrate. Final catalyst compositions in atomic ratio were: 100Fe/4.6Si/0.36K, 100Fe/4.6Si/1.4K and 100Fe/4.6Si/2.2K.

Reaction System

A 1-liter autoclave operated as a continuous stirred tank reactor (CSTR) was used for the slurry FTS reactions. Analysis of the gaseous, liquid and solid (at room temperature) products was conducted both on- and off-line using a variety of gas chromatographs. More details of the reaction system used and product analysis have been reported previously (8).

Procedure

Approximately 5 g of catalyst was mixed with 300 g of melted octacosane (purified to remove halogens) in the CSTR. The reactor pressure was increased to 13.1 MPa with carbon monoxide at a flow rate of 13 NL h^{-1} (20 $^{\circ}$C, 0.10 MPa). The reactor temperature was increased to 270 $^{\circ}$C at a rate of 120 $^{\circ}$C h^{-1}. These activation conditions were maintained for 24 h.

At the end of the activation period, synthesis gas flow was started at a H_2/CO ratio of 0.67. During the entire run the reactor temperature was 270^{o}C, the pressure was 13.1 MPa and the stirring speed was maintained at 750 rpm. About two days were required before the catalyst reached steady state as evidenced by the constant conversion of synthesis gas. Subsequently, the space velocity of the synthesis gas was varied between 5 and 65 NL h^{-1} g-Fe^{-1}. The conversions of carbon monoxide, hydrogen, and the formation of various products were measured with a period of approximately 24 hours at each space velocity. The H_2/CO ratio of the feed synthesis gas was kept constant at 0.67 at all the space velocities. Periodically during the run, the catalyst activity was measured at pre-set "standard" conditions (a space velocity of 10 NL h^{-1} g-Fe^{-1}) to check for catalyst deactivation.

RESULTS

The results for three potassium levels (0.36, 1.4 and 2.2) are presented. Representative runs for the 0.36 K and 1.4 K catalysts lasted for 500 hours during which the catalyst activity was constant as measured at pre-set "standard" conditions. Preliminary data for the 2.2 K catalyst showed that this catalyst deactivated after about 250 hours of time on stream. Hence, data for this catalyst were obtained in multiple runs lasting for a maximum of 250 hours. The synthesis gas conversion as measured in multiple runs was accurate to about +/- 1.5%.

Conversions

The syngas conversion is a rough measure of the overall Fischer-Tropsch activity of an iron-based catalyst. The syngas conversion for the three levels of potassium studied is shown in Figure 1. It is immediately evident that the trends in synthesis gas conversion with potassium loading are dependent on the space time (reaction time) or the conversion level. At low synthesis gas conversion levels or low space times, the catalyst with the lowest potassium loading (0.36 K) exhibited the highest synthesis gas conversion. At intermediate conversion levels, the catalyst with an intermediate potassium loading (1.4 K) exhibited the highest synthesis gas conversion. At the highest conversion levels, the synthesis gas conversion exhibited by all three of the catalysts closely approached each other.

This is more clearly shown in Figure 2 where the synthesis gas conversion is plotted against potassium loading at various space velocities. At high space velocities, potassium appears to act as a catalyst poison. At the lowest space velocities, potassium appears to slightly enhance the synthesis gas conversion. At intermediate space velocities, there appears to be an optimum potassium level for maximum synthesis gas conversion.

The same trends obtained for synthesis gas conversion are also evident for the hydrocarbon production rate with potassium loading (Figure 3). This confirms that synthesis gas conversion is a good measure of the overall FTS activity.

Product/Reactant Partial Pressures

The partial pressure of water is an important parameter in the FTS. Water has been shown to inhibit the FTS reaction rate (Equation 3). As shown in Figure 4, the partial pressure of water in the reactor exhibits the behavior of a reaction intermediate, i.e., the water partial pressure is high initially and then decreases with reaction time. This is not surprising as the water formed by the FTS can be subsequently consumed in the WGS reaction. In general, the partial pressure of water in the reactor decreases with potassium loading.

The reaction rate expression given in Equation (3) can be rearranged as

$$-4_{CO+H_\|} = \frac{kP_{H_\|}}{1 + b\left(\frac{P_{H_\|O}}{P_{CO}P_{H_\|}}\right)} \qquad \textbf{(4)}$$

In contrast to the water partial pressure, the value of the partial pressure ratio,

$$\frac{P_{H_2O}}{P_{CO}P_{H_2}}$$

increases monotonically with reaction time as shown in Figure 5. The value of the partial pressure ratio increases, in general, with potassium loading.

Reaction Rates of FTS and WGS

The individual rates of reaction of the FTS (r_{FTS}) and WGS (r_{WGS}) can be calculated from experimentally observed quantities by:

$$r_{WGS} = r_{CO_2} \tag{5}$$

and

$$r_{FTS} = r_{CO} - r_{CO_2} \tag{6}$$

where r_{CO_2} is the rate of carbon dioxide formation and r_{CO} is the rate of carbon monoxide conversion.

These calculated rates of the two reactions are shown in Figure 6 for the three potassium levels. At low reaction times, the rate of the FTS is much greater than the rate of the WGS reaction; however, the rate of the WGS reaction closely approaches the rate of the FTS at high reaction times. The trends in the FTS rate at different potassium loadings are similar to the variation of synthesis gas conversions with potassium loading (Figure 1).

At low reaction times, there are marked differences between the WGS reaction rates for different potassium loadings. The catalyst with intermediate potassium loading (1.4 K) exhibits the highest WGS reaction rate at the low reaction times; however, at high reaction times the rates of the WGS for the three potassium loadings are quite similar.

Extent of WGS

One measure of the extent of the WGS reaction can be obtained by following the WGS reaction quotient (RQ_{WGS}).

$$RQ_{WGS} = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \tag{7}$$

As shown in Figure 7, the value of the reaction quotient is small at low carbon monoxide conversions and increases considerably at higher carbon monoxide conversions. The value of the reaction quotient increases with potassium loading at the same carbon monoxide conversions. Hence, the extent of the WGS reaction measured in this way appears to increase with potassium loading.

The FTS reaction produces water which is a necessary reactant for the WGS reaction to proceed. Thus the rate/extent of the WGS reaction is limited by the amount of water formed by the FTS. Since water is not supplied to the reactor, the stoichiometry of the FTS and WGS reactions (Equations (1) and (2)) dictates that

$$r_{WGS} < or = r_{FTS} \tag{8}$$

Hence, a more reliable measure of the extent of the WGS reaction is to compare the relative rate of the WGS to the rate of the FTS to see how closely the rate of the WGS approaches that of the FTS. As shown in Figure 8, the ratio of the FTS rate to the WGS reaction rate increases with carbon monoxide conversion and approaches a value of one. This is consistent with the data shown in Figures 6 and 7. Figure 8 clearly shows that the extent of the WGS reaction increases substantially with potassium loading at carbon monoxide conversions less than 80%. However, at high carbon monoxide conversions the increase in the extent of the WGS reaction with potassium loading is small.

Kinetics

The reaction rate expression given in Equation (3) can be linearized by rearrangement as

$$\frac{P_{H_2}}{-r_{CO-H_2}} = \frac{1}{k} + \frac{b}{k}\,\frac{P_{H_2O}}{kP_{CO}P_{H_2}} \qquad \textbf{(9)}$$

Hence a plot of $\frac{P_{H_2}}{-r_{CO+H_2}}$ versus $\frac{P_{H_2O}}{P_{CO}P_{H_2}}$ should give a straight line whose intercept is given by (1/k) and whose slope is given by (b/k).

The data for the three potassium loadings studied are plotted in this manner in Figure 9. It is evident that the results do not lie on a single straight line for any of the catalysts studied. The regression lines shown in Figure 9 have been drawn through the data obtained at low conversions. This situation is analyzed in the Discussion section.

Alkene Selectivity

Figure 10 illustrates the alkene selectivity of the light hydrocarbon products (C_2 and C_3) obtained. Both the C_2 and C_3 alkene selectivities decrease with carbon monoxide conversion for all the catalysts studied. The selectivity to C_2 alkene increases with potassium loading at similar carbon monoxide conversions. This is true over the entire range of carbon monoxide conversions obtained in this study. However, the effect of increasing potassium amounts on the selectivity to C_3 alkenes depends on the carbon monoxide conversion level; at lower carbon monoxide conversions the highest alkene selectivity is obtained over the 0.36 K catalyst, while at higher conversions the highest alkene selectivity is exhibited by the 1.4 K and 2.2 K catalysts.

1-Alkene Selectivity

The isomerization ability at different potassium levels can be compared from the selectivity of the 1-alkene relative to the total alkenes (1-alkene + cis-2-alkene + trans-2-alkene) produced. This is illustrated for the butenes in Figure 11 for the three potassium levels as a function of carbon monoxide conversion. The selectivity to 1-butene decreases with increasing carbon monoxide conversion and increases with increasing potassium loading at similar carbon monoxide conversions.

Methane Selectivity

As shown in Figure 12, the methane selectivity was constant and similar for all the catalysts studied at low carbon monoxide conversions. Above 50% carbon monoxide conversion, the methane selectivity increased with increasing conversion. The selectivity to methane increased with decreasing potassium loading.

DISCUSSION

Effect of Increase in Potassium on WGS and FTS

For synthesis gas with a low H_2/CO ratio, the extent and/or rate of the WGS is extremely important to achieve a high conversion of carbon monoxide. For example, if there was no WGS, then according to Equations (1) and (2) the maximum carbon monoxide conversion would be 31%, assuming $n = 2.3$ (actual values of n or the average H/C ratio of the hydrocarbon products are between 2.2 and 2.4). In the case of all three of the catalysts studied, there is always some accompanying WGS reaction. In order to illustrate the importance of a high WGS reaction rate, it is necessary to calculate the rate of hydrogen consumed by the FTS reaction. This can be calculated from the stoichiometry of the FTS (Equation 1) as

$$H_2 \ consumed \ by \ FTS = r_{FTS}(1 + (n/2)) \tag{10}$$

Figure 13 shows a comparison of the hydrogen consumed by the FTS and the hydrogen supplied to the reactor for the three potassium loadings as a function of reaction time. The hydrogen supplied to the reactor varies with space velocity and is the same for each catalyst at the same space velocity. The hydrogen supplied to the reactor is sufficient for the FTS up to a space time of about 0.07 to 0.09 h g(Fe) NL^{-1}; however, at higher space times (or reaction times) the hydrogen supplied to the reactor is lower than that consumed by the FTS. The extra hydrogen consumed by the FTS must be formed by the WGS reaction.

The same data can be plotted with respect to carbon monoxide conversion instead of reaction time (Figure 14). The hydrogen supplied to the reactor is now different for each catalyst as the carbon monoxide conversions are different at the same space velocities. Similar to Figure 13, the hydrogen supplied to the reactor is sufficient for the FTS at low carbon monoxide conversions (less than 50%). Further, at higher carbon monoxide conversions, part of the hydrogen needed by the FTS must be obtained from the WGS reaction due to the insufficient hydrogen supply to the reactor. This illustrates that a high rate of the WGS reaction is necessary to supply the extra hydrogen in order to have a high rate of the FTS for synthesis gas containing a low H_2/CO ratio.

There is an increasing need for hydrogen formed by the WGS reaction with increasing carbon monoxide conversion (Figure 14). Further, the extent of the WGS reaction increases substantially with potassium loading (Figure 8). These two factors can explain the variation in the effect of potassium on synthesis gas conversion (or activity) with reaction time (Figure 2).

At low carbon monoxide conversions or reaction times the extent/rate of the WGS reaction is not critical. The hydrogen supplied to the reactor is more than sufficient for the FTS. At these conversion levels, the only determinant of the overall FTS activity is the FTS reaction (Equation 1). As shown in Figure 2, the overall FTS activity of the catalyst (given by the synthesis gas conversion) decreases with potassium loading. Hence, potassium apparently acts as a catalyst poison for the FTS reaction.

As the carbon monoxide conversion increases, the extent/rate of the WGS becomes increasingly critical. The overall FTS activity is increasingly dependent on the hydrogen formed by, and thus the rate of, the WGS reaction. The overall FTS activity is then determined not only by the FTS reaction (Equation 1) but also by the WGS reaction (Equation 2). The highest overall FTS activity (synthesis gas conversion) at intermediate carbon monoxide conversions should then be exhibited by a catalyst which has an acceptably high rate for both the FTS reaction (Equation 1) as well as the WGS reaction (Equation 2). Since, the extent of the WGS reaction increases with potassium loading, the overall FTS activity should be a maximum at intermediate potassium loadings at these intermediate carbon monoxide conversions levels. This is exactly the situation at intermediate carbon monoxide conversion levels (Figure 2) where the synthesis gas conversion is the highest for the catalyst with an intermediate potassium loading (1.4 K).

At high carbon monoxide conversions, the overall FTS activity is increasingly dominated by the WGS reaction rather than the FTS reaction. Hence, the overall FTS activity should be higher for catalysts having a high rate for the WGS reaction. Since the extent of the WGS reaction increases with potassium loading, this implies that the overall FTS activity should be the highest for the catalyst with the highest potassium content. As shown in Figure 2, at high carbon monoxide conversions the synthesis gas conversion is maximum for the 2.2 K catalyst.

In summary, the above reasoning provides a consistent explanation for the experimental results of varying optimum potassium loadings with space velocity (Figure 2). According to this explanation, potassium actually inhibits the rate of the FTS reaction (Equation 1). Varying optimum potassium loadings with synthesis gas conversion level are due to the enhancement of the WGS reaction by potassium.

Effect of Water Partial Pressure

The partial pressure of water or the ratio of the partial pressure of water to the product of the partial pressures of carbon monoxide and hydrogen inhibit the FTS rate according to Equation (3). A possible explanation for changes in catalyst activity with potassium loading is the corresponding change in the water partial pressure or the partial pressure ratio with potassium loading. However, a comparison of Figures 4 or 5 with Figure 1 does not show any correlation between the partial pressures and synthesis gas conversion for the three potassium loadings studied. For instance, the water partial pressure decreases with potassium loading at the same space velocity whereas the synthesis gas conversion does so only at high space velocities and does not at low and intermediate space velocities.

Effect of Potassium on Kinetic Parameters

Figures 13 and 14 clearly show that the FTS reaction must depend increasingly on the hydrogen formed by the WGS reaction as the reaction time or carbon monoxide conversion increases. Thus the overall FTS rate is increasingly affected by the rate/extent of the WGS reaction at high conversions. Only at lower conversions is the overall FTS rate unaffected by the WGS reaction. Hence, there is a change in the rate limiting step of the overall FTS reaction (Equation 1 or Equation 2) with carbon monoxide conversion. This provides an explanation for the non-linearity of the experimental results when plotted (Figure 9) according to the linearized version of Equation 3. The results at carbon monoxide conversions of less than 60% lie on a straight line; however, results at higher carbon monoxide conversions deviate substantially.

Since, the rate of the FTS reaction is of importance in this study, regression lines have been drawn in Figure 9 for the data at carbon monoxide conversions below 60%. Information obtained from these regression lines then correspond only to the FTS reaction (Equation 1) and not to any influence of the WGS reaction (Equation 2). The intercept and slope of the regression lines can be used to calculate the rate constant (k) and the adsorption parameter (b) with potassium loading.

The rate constant (k) decreases with potassium loading as shown in Figure 15. This decrease in the rate constant is more than an order of magnitude between loadings of 0.36 K and 2.2 K. This result is consistent with the explanation offered for varying optimum potassium loadings with conversion level wherein the potassium was shown to be a poison or decrease the catalyst activity for the FTS reaction (Equation 1).

The adsorption parameter (b) also decreases with potassium loading as shown in Figure 16. Similar to the extent of decrease in the rate constant, the adsorption parameter decreases by over an order of magnitude between 0.36 K and 2.2 K loadings. The adsorption parameter has been shown to be given by (5)

$$b = \frac{K_{H_2O}}{K_{CO}} \tag{11}$$

where K_{H_2O} and K_{CO} are adsorption equilibrium constants for water and carbon monoxide respectively. Thus a decrease in the adsorption parameter (b) can be due to a decrease in the adsorption equilibrium constant for water and/or an increase in the adsorption equilibrium constant for carbon monoxide. Several previous studies (3,9,10) have shown that potassium causes an increase in the adsorption equilibrium constant for carbon monoxide. The observed decrease in the adsorption parameter (b) with potassium loading is consistent with the results of these studies.

A decrease in the rate constant (k) with potassium loadings implies a decrease in the FTS rate with potassium loading. In contrast, a decrease in the adsorption parameter (b) with potassium loading implies an increase in the FTS rate with potassium loading. This provides a possible explanation for a maximum in FTS activity with potassium loading. Thus an optimum potassium loading would be one for which the rate constant (k) is not too low and the adsorption parameter (b) not too high.

Effect of Potassium on Selectivity

As illustrated in Figure 10, increasing the amount of potassium on the catalyst appears to increase the selectivity to ethene. This is in conformity to previous studies. However, the selectivity to propene depends on the carbon monoxide conversion level.

This is in contrast to previous studies and illustrates the importance of comparing selectivities at similar carbon monoxide conversion.

Since the selectivity to 1-butene relative to total butenes increases with increasing potassium loading (Figure 11), the isomerization ability of the catalyst decreases with increasing amounts of potassium. Similarly, the selectivity to methane decreases with increasing potassium loading at carbon monoxide conversions greater than 50%.

CONCLUSION

A systematic evaluation of the effect of potassium on FTS activity and selectivity has been carried out in this study. A major observation of this study is that the trends in FTS activity with potassium loading are dependent on the space velocity and synthesis gas conversion level. At low synthesis gas conversions, the FTS activity decreases with potassium loading. At intermediate synthesis gas conversions, there is a maximum in FTS activity with potassium loading. At high synthesis gas conversions, potassium slightly enhances the FTS activity.

A consistent explanation for these activity trends has been given. The overall FTS activity is independent of the WGS reaction at low synthesis gas conversions. Potassium acts as a catalyst poison at these conversion levels as the FTS activity decreases with potassium loading. As the synthesis gas conversion increases, the hydrogen supplied to the reactor is insufficient for the FTS and the FTS increasingly depends on the hydrogen formed by the WGS reaction. Further, the extent of the WGS reaction increases with potassium loading. Thus as synthesis gas conversion increases the maximum overall FTS activity is obtained first at intermediate potassium loadings and finally at the highest potassium loading used in this study.

The effect of potassium on kinetic parameters for the FTS has also been determined in this study. The FTS activity depends on a rate constant and an adsorption parameter according to a previously proposed rate expression (5). The rate constant decreases by more than an order of magnitude when the potassium loading is increased from 0.36 K to 2.2 K. Thus potassium acts as a catalyst poison for the FTS. The adsorption parameter also decreases by over an order of magnitude with increasing potassium loadings between 0.36 K and 2.2 K. Since decreases in the rate constant and the adsorption parameter affect the FTS rate in opposite directions, these results provide a reasonable explanation for a maximum in FTS activity with potassium loading. Hence, an optimum potassium loading is one for which the rate constant is not too low and the adsorption parameter not too high.

Unlike previous studies, the effect of potassium on catalyst selectivity has been compared at similar conversions. The effect of increasing amounts of potassium on alkene selectivity depends on the number of carbon atoms of the hydrocarbons as well as the carbon monoxide conversion level. The extent of isomerization decreases with potassium loading. The selectivity to methane in the total hydrocarbon product is affected by potassium at carbon monoxide conversions above 50% and increases with decreasing potassium loading.

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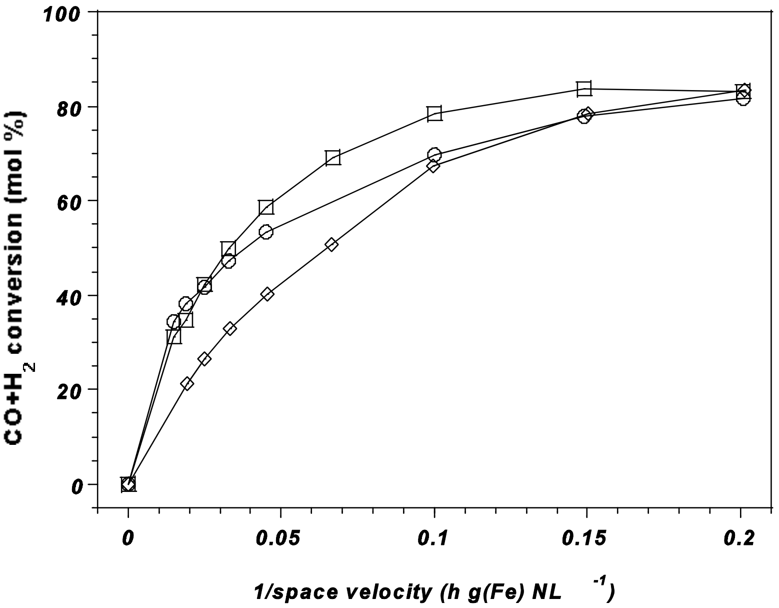

Figure 1. Synthesis gas conversion as a function of potassium loading. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

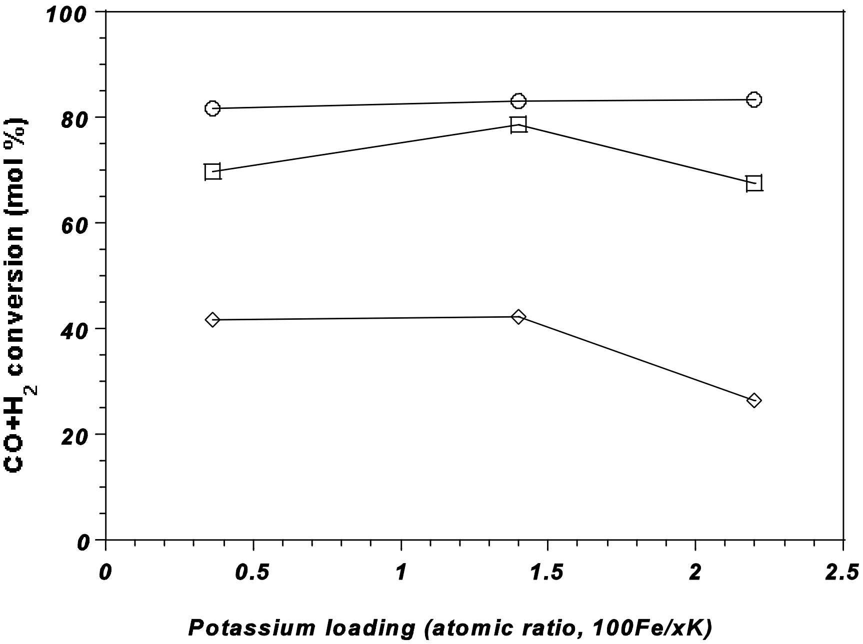

Figure 2. Synthesis gas conversion as a function of potassium loading. (○) 5 NL h^{-1} g(Fe)$^{-1}$, (□) 10 NL h^{-1} g(Fe)$^{-1}$ and (◊) 50 NL h^{-1} g(Fe)$^{-1}$.

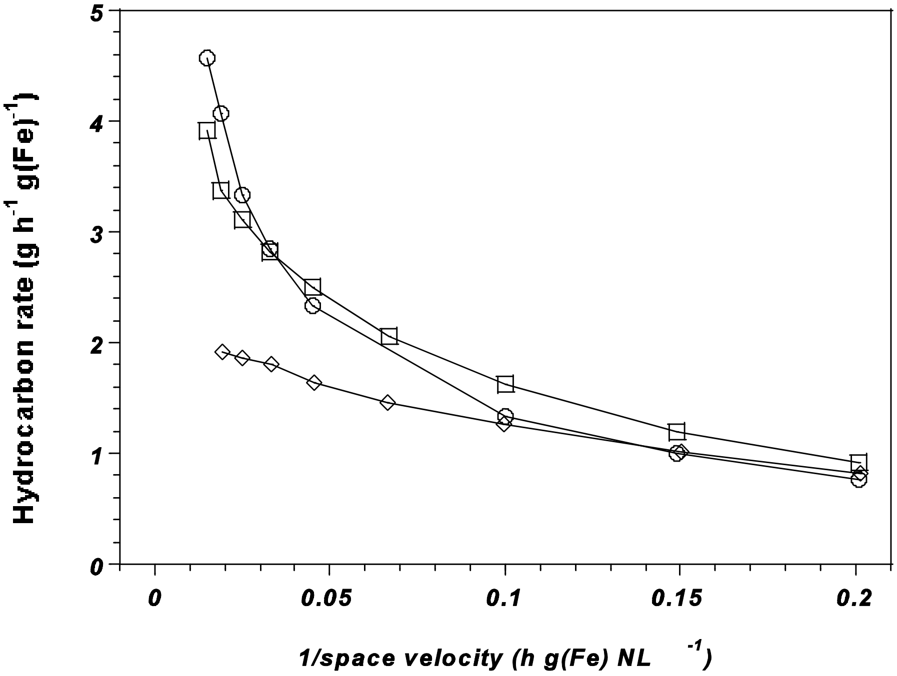

Figure 3. Hydrocarbon production rate as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

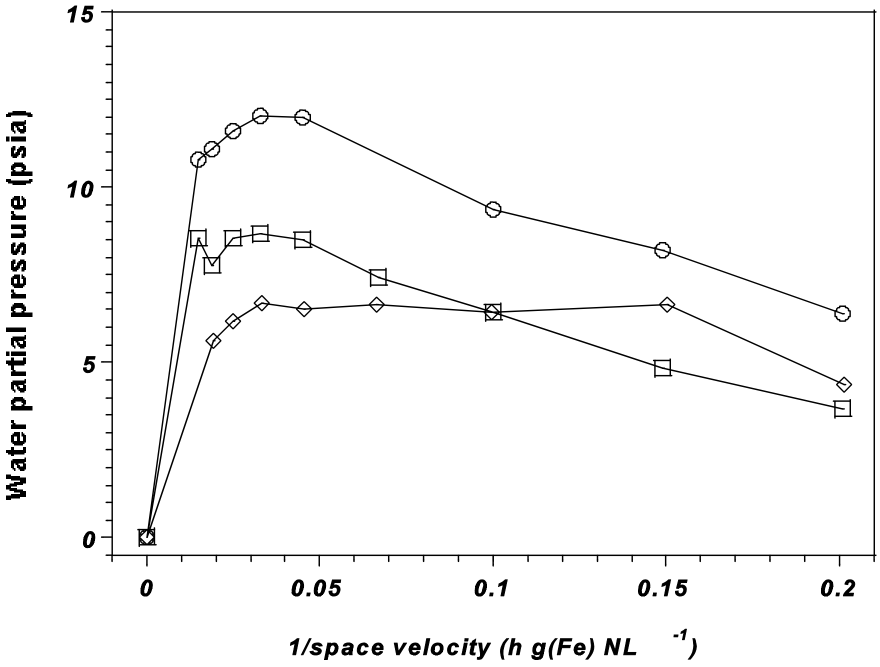

Figure 4. Water partial pressure as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

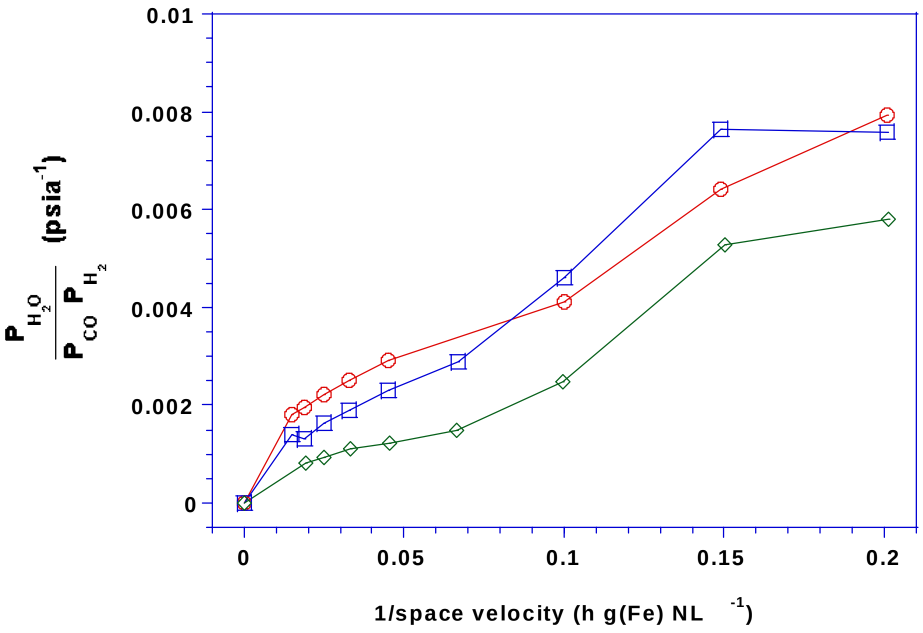

Figure 5. Partial pressure ratio, $\frac{P_{H_2O}}{P_{CO}P_{H_2}}$ (psia^{-1}) as a function of reciprocal flow rate 1/space velocity (h g(Fe)NL^{-1}). (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

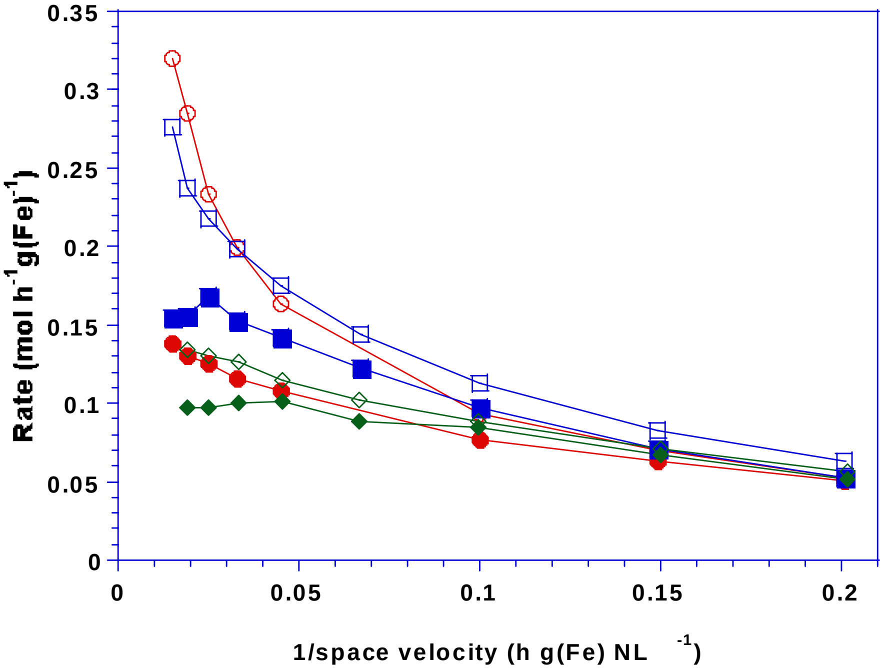

Figure 6. Fischer-Tropsch (open symbols) and water-gas shift (closed symbols) rates as a function of reciprocal flow rate. (○) FT; 0.36 K, (●) WGS; 0.36 K, (□) FT; 1.4 K, (■) WGS; 1.4 K, (◊) FT; 2.2 K, and (◆) WGS; 2.2 K.

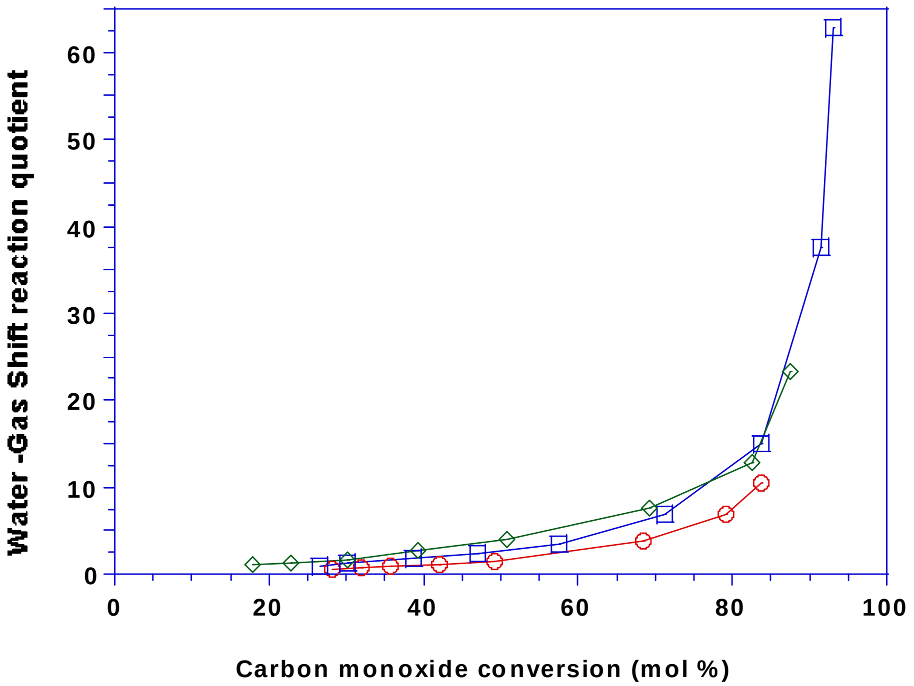

Figure 7. Water-gas shift reaction quotient as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

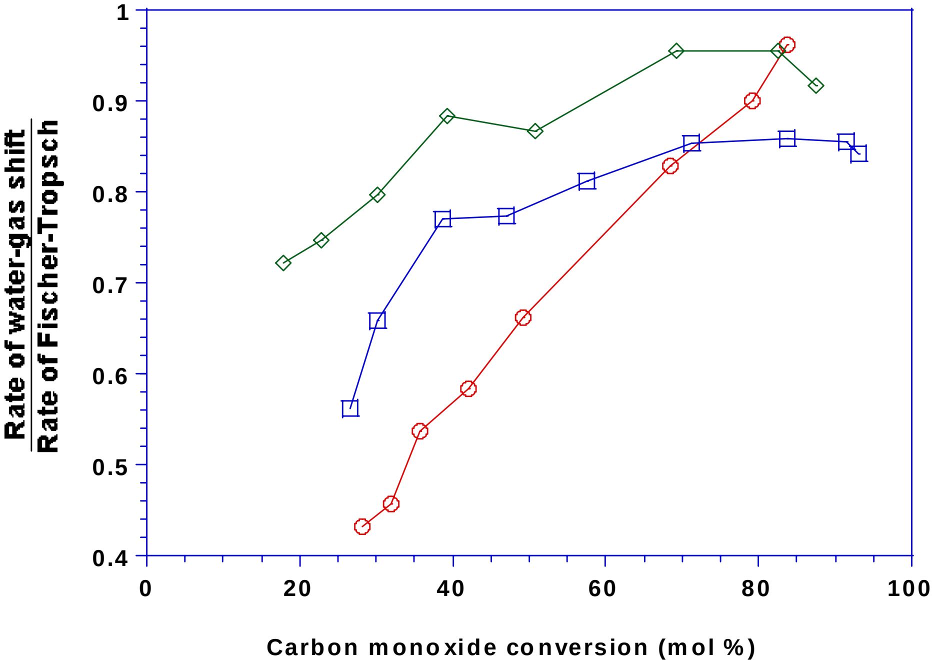

Figure 8. Ratio of rate of Fischer-Tropsch synthesis to rate of water-gas shift reaction as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

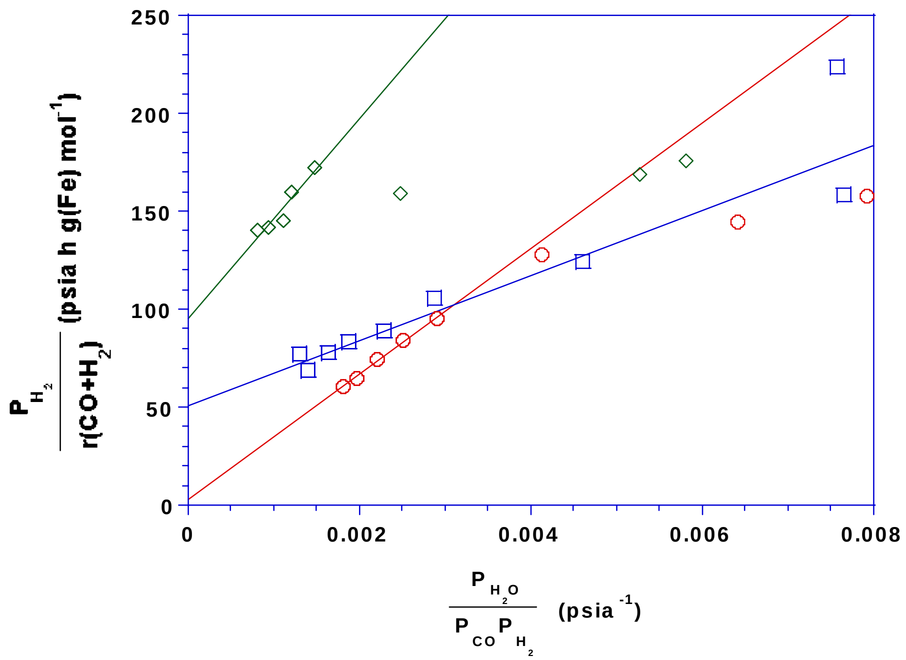

Figure 9. Plots of the linearized version of equation 3. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

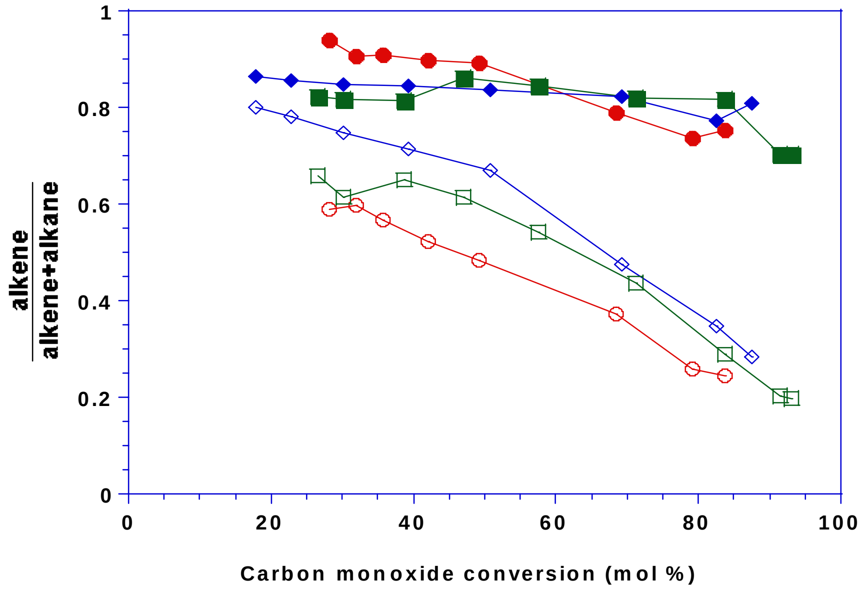

Figure 10. Alkene selectivity of C_2 (open symbols) and C_3 (closed symbols) hydrocarbons. (○) C_2; 0.36 K, (●) C_3; 0.36 K, (□) C_2; 1.4 K, (■) C_3; 1.4 K, (◇) C_2; 2.2 K, and (◆) C_3; 2.2 K.

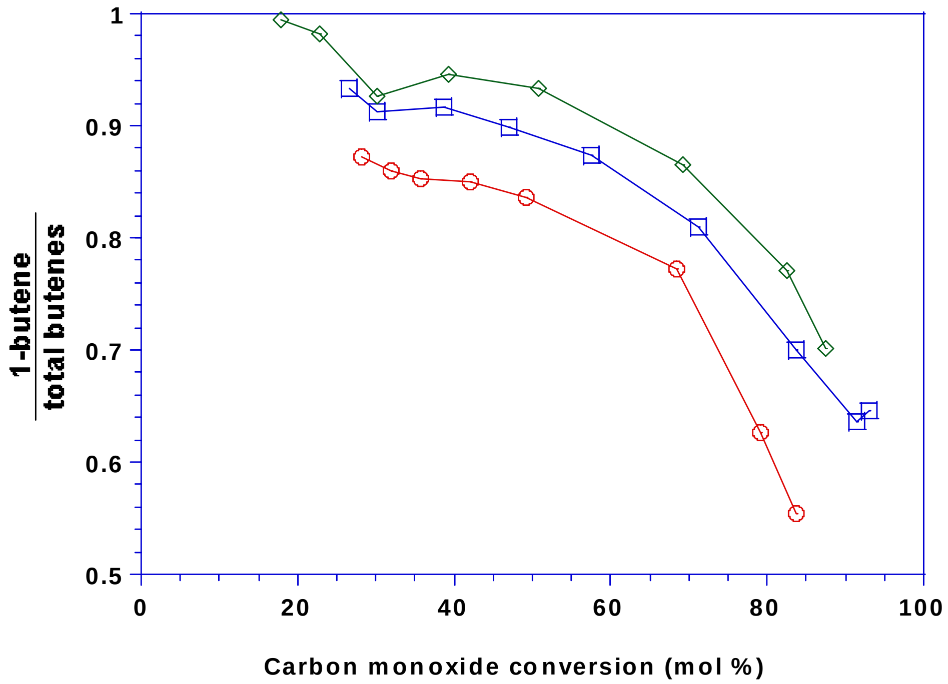

Figure 11. Fraction of 1-butene in total linear alkenes as a function of carbon monoxide conversion. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

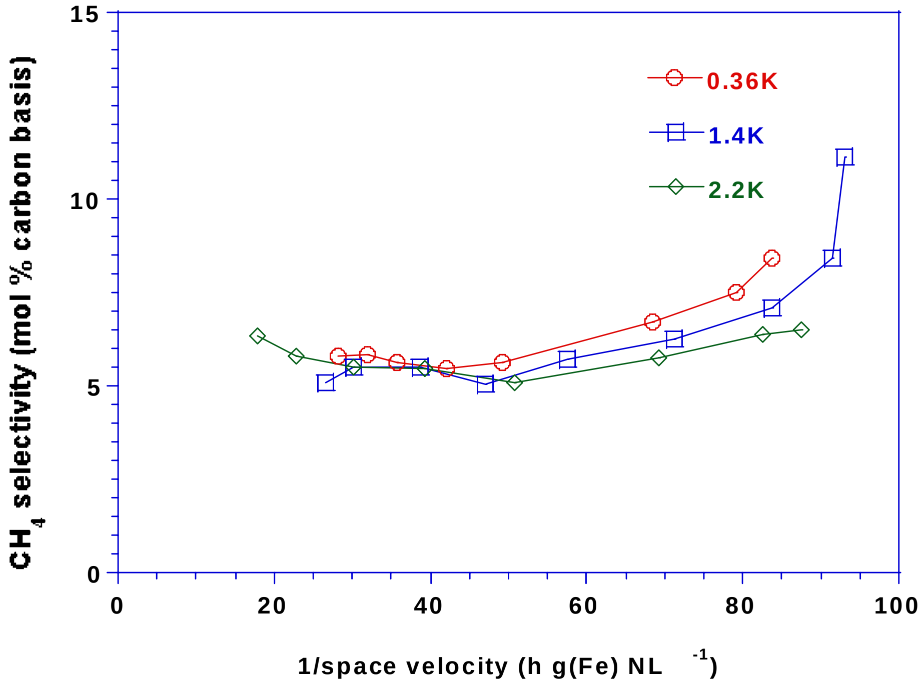

Figure 12. Methane selectivity as a function of carbon monoxide conversion. (○) 0.36 K, (□) 1.4 K, and (◊) 2.2 K.

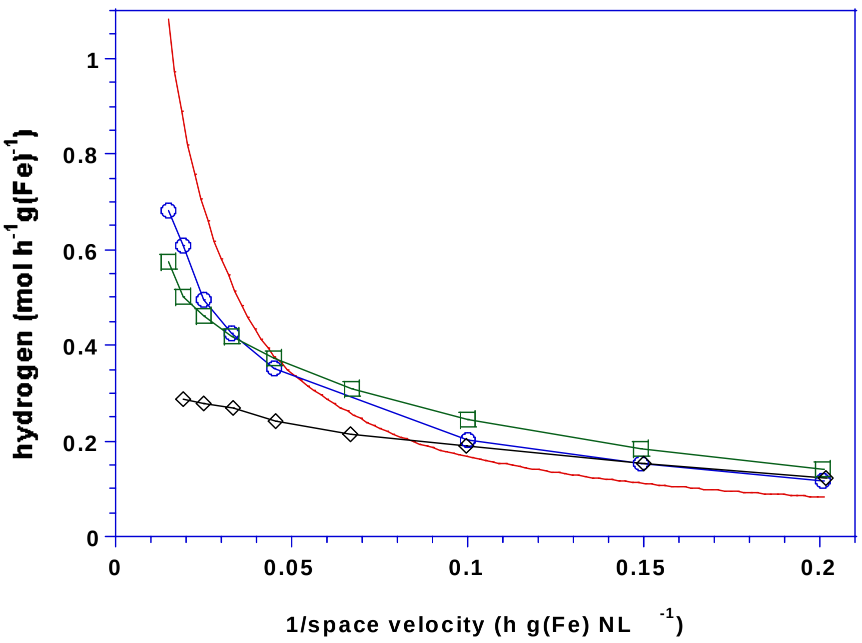

Figure 13. Need for water-gas shift reaction shown as a comparison of hydrogen supplied to the reactor and hydrogen used by the FTS. (—) hydrogen supplied to reactor, (○) hydrogen used by 0.36 K catalyst, (□) hydrogen used by 1.4 K catalysts, and (◊) hydrogen used by 2.2 K catalyst.

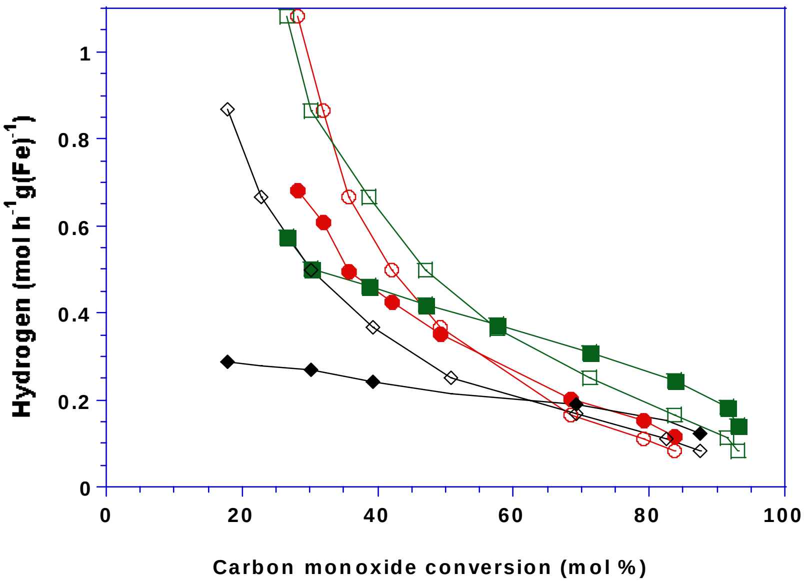

Figure 14. Need for water-gas shift reaction with increasing carbon monoxide conversion. Open symbols: hydrogen supplied to reactor. Closed symbols: hydrogen used by FTS. (○, ●) 0.36 K, (□, ■) 1.4 K, and (◊,◆) 2.2 K.

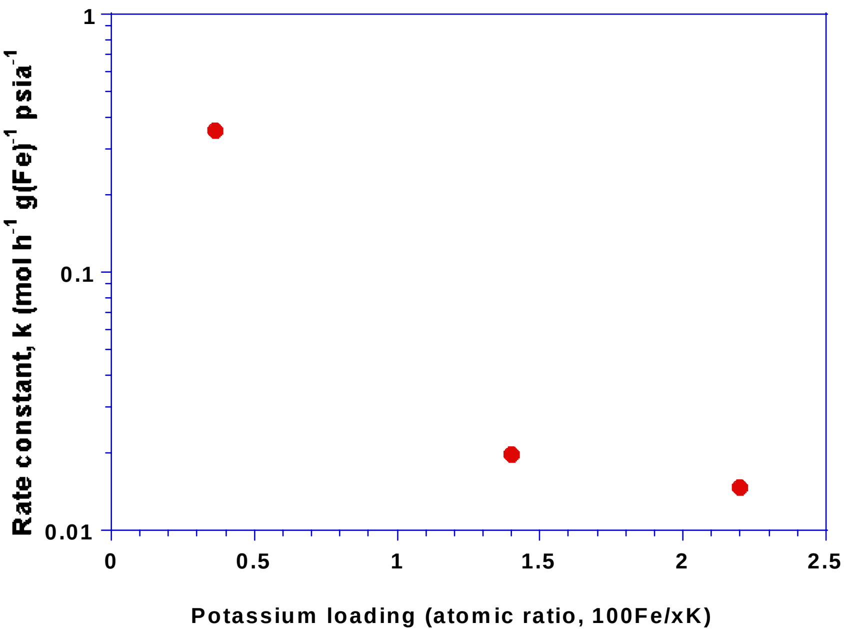

Figure 15. Fischer-Tropsch rate constant as a function of potassium loading.

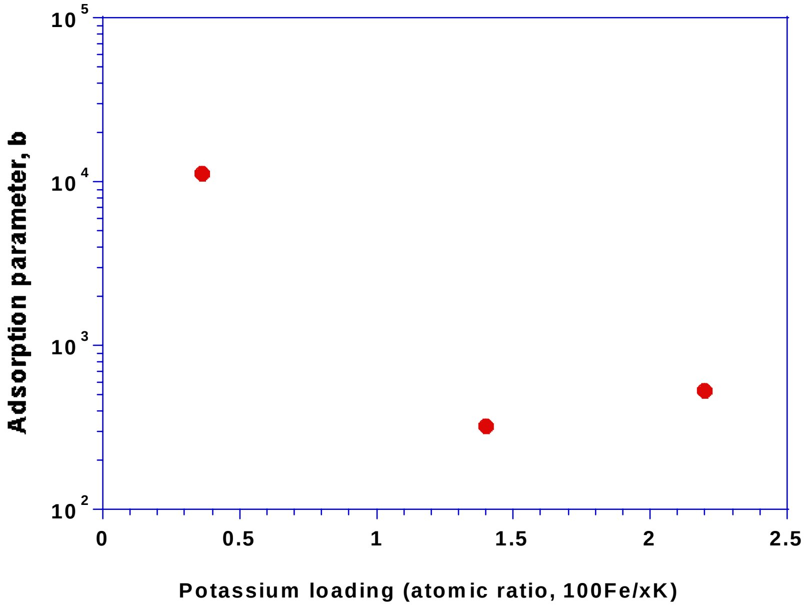

Figure 16. Adsorption parameter (b) from equation 3 as a function of potassium loading.