

# Effect of Potassium Promotion on Iron-Based Catalysts for Fischer–Tropsch Synthesis<sup>1</sup>

Ajoy P. Raje, Robert J. O'Brien, and Burtron H. Davis

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, Kentucky 40511

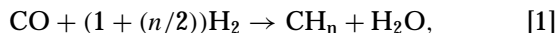
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The effect of potassium on Fischer–Tropsch catalyst activity, kinetic parameters, and selectivity has been investigated for a precipitated iron catalyst that was employed with low H<sub>2</sub>/CO ratio synthesis gas. A wide range of synthesis gas 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 of synthesis gas conversion. As potassium loading increased, the catalyst activity either decreased (low conversion), passed through a maximum (intermediate conversion), or increased (high conversion). 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 1-alkene product decreased with potassium loading, while the selectivity to methane decreased only slightly with increasing potassium content at CO conversions about 50% and higher. © 1998

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## INTRODUCTION

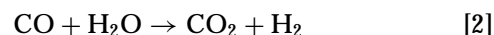
The Fischer–Tropsch Synthesis (FTS) converts synthesis gas, a mixture of carbon monoxide and hydrogen, to hydrocarbons. The FTS reaction can be represented as



where  $n$  is the average H/C ratio of the hydrocarbons produced. Iron-based catalysts also possess activity for the water-gas shift (WGS) reaction. This property allows the direct processing of synthesis gas with a low H<sub>2</sub>/CO ratio (as produced by coal gasification in advanced gasifiers) without

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an additional WGS reactor. The WGS reaction



utilizes water produced during FTS to produce additional hydrogen for FTS.

Typical iron-based catalysts contain small amounts of potassium (chemical promoter) along with binders (structural promoters) 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

$$-r_{\text{CO}+\text{H}_2} = \frac{k P_{\text{CO}} P_{\text{H}_2}^2}{P_{\text{CO}} P_{\text{H}_2} + b P_{\text{H}_2\text{O}}}. \quad [3]$$

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 have a major effect on the FTS activity, especially for a low H<sub>2</sub>/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. This study has been conducted under conditions typical for a low- $\alpha$  catalyst and operating conditions for a slurry reactor. 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 100 Fe/4.6 Si/0.36 K, 100 Fe/4.6 Si/1.4 K, and 100 Fe/4.6 Si/2.2 K.

### 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 1.31 MPa with carbon monoxide at a flow rate of 13 NL h<sup>-1</sup> (20°C, 0.10 MPa). The reactor temperature was increased to 270°C at a rate of 120°C h<sup>-1</sup>. These activation conditions were maintained for 24 h.

At the end of the activation period, synthesis gas flow was started at a H<sub>2</sub>/CO ratio of 0.67. During the entire run the reactor temperature was 270°C, the pressure was 1.31 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<sup>-1</sup> g-Fe<sup>-1</sup>. The conversion of carbon monoxide and hydrogen and the formation of various products were measured with a period of approximately 24 h at each space velocity. The H<sub>2</sub>/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 preset "standard" conditions (a space velocity of 10 NL h<sup>-1</sup> g-Fe<sup>-1</sup>) to check for catalyst deactivation.

The water partial pressure was determined by collecting the water in the traps, separating it from the oil, and determining its amount by weighing. The water in the exit gas from the 0°C trap was calculated and this amount have been added to the weight of liquid water collected in the traps. The weight of water, the exit gas flow being known, has been converted to partial pressure in the reactor based upon the ideal gas law.

## 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 h 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 h of time on stream. Hence, data for this catalyst were obtained in multiple runs lasting for a maximum of 250 h. The synthesis gas conversion as measured in multiple runs was accurate to about  $\pm 1.5\%$ .

### 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 Fig. 1. It is immediately evident that the trends in synthesis gas conversion with potassium loading are dependent on the space 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

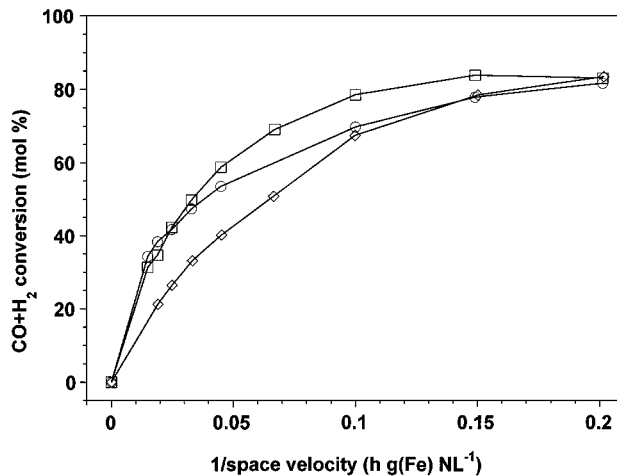


FIG. 1. Synthesis gas conversion as a function of reciprocal flow rate.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

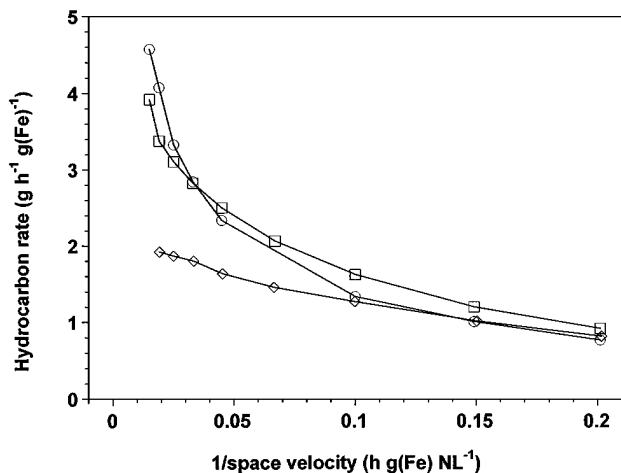


FIG. 2. Hydrocarbon production rate as a function of reciprocal flow rate.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

conversion. At the highest conversion levels, the synthesis gas conversion exhibited by all three of the catalysts closely approached each other. Moreover, the rate of CO conversion becomes slower at larger space times. Thus, at high space velocities, potassium appears to act as a mild 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 (Fig. 2). 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 (Eq. [3]). As shown in Fig. 3, the partial pressure of

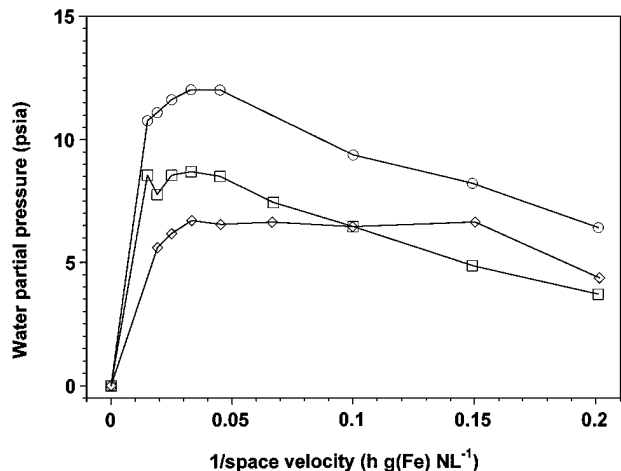


FIG. 3. Water partial pressure as a function of reciprocal flow rate.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

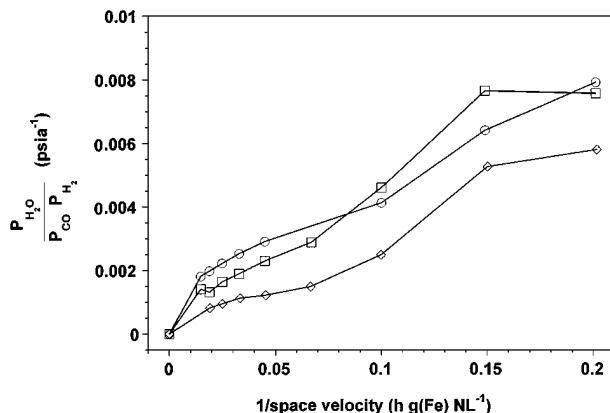


FIG. 4. Partial pressure ratio,  $P_{H_2O}/P_{CO}P_{H_2}$ , as a function of reciprocal flow rate.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

water in the reactor exhibits the behavior of a reaction intermediate; i.e., the water partial pressure initially increases to a maximum 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 is lower as the potassium loading increases. At the higher CO conversion levels, the WGS reaction approaches the equilibrium value. Thus, the water partial pressure in the reactor shows little dependence on catalyst at high CO conversion levels.

The reaction rate expression given in Eq. [3] can be rearranged as

$$-r_{CO+H_2} = \frac{kP_{H_2}}{1 + b(P_{H_2O}/P_{CO}P_{H_2})}. \quad [4]$$

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 (Fig. 4). At the shorter space times the value of the partial pressure ratio decreases, in general, with potassium loading; at higher space times the approach to equilibrium becomes a dominant factor.

#### 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

$$r_{WGS} = r_{CO_2} \quad [5]$$

and

$$r_{FTS} = r_{CO} - r_{CO_2}, \quad [6]$$

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

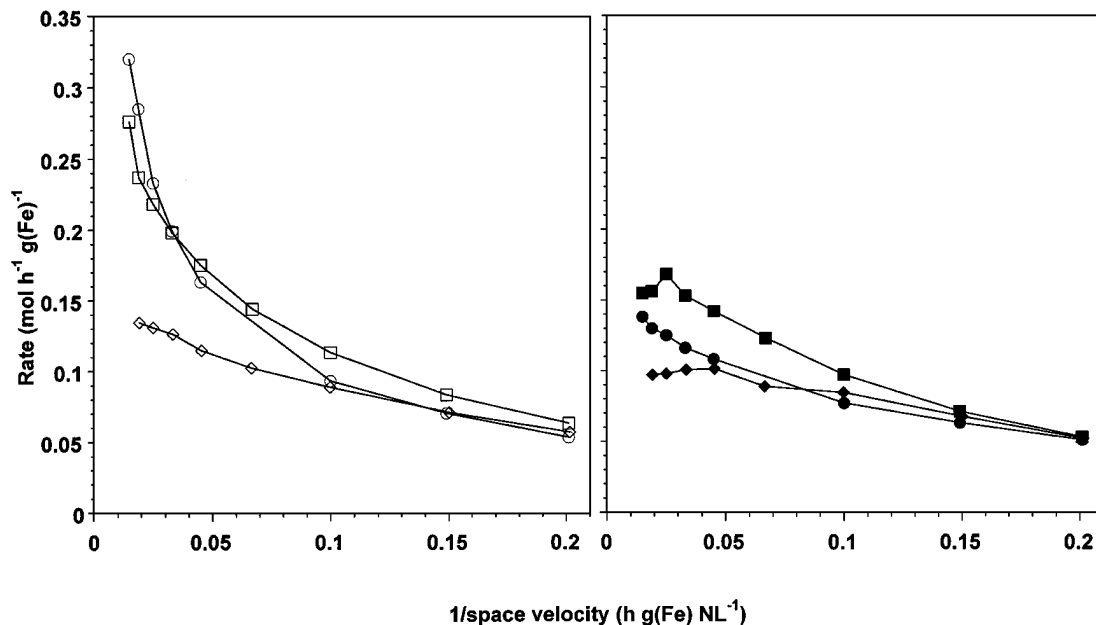


FIG. 5. Fischer-Tropsch (open symbols) and water-gas shift (closed symbols) rates as a function of reciprocal flow rate.  $\circ$ , FT, 0.36 K;  $\bullet$ , WGS, 0.36 K;  $\square$ , FT, 1.4 K;  $\blacksquare$ , WGS, 1.4 K;  $\diamond$ , FT, 2.2 K; and  $\blacklozenge$ , WGS, 2.2 K.

The calculated rates of the two reactions are shown (Fig. 5) for three potassium levels. At low reaction times, the rate of the FTS is greater than the rate of the WGS reaction; however, as the potassium level increases these two rates become more nearly the same at short residence times. The rate of the WGS reaction closely approaches the rate of the FTS at high reaction times.

At low reaction times, there are small, but significant, 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 ( $RQ_{\text{WGS}}$ ),

$$RQ_{\text{WGS}} = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}. \quad [7]$$

As shown in Fig. 6, the value of the reaction quotient is small at low carbon monoxide conversions and increases at higher carbon monoxide conversions, especially at CO conversions above about 85%. The value of the reaction quotient shows only a small dependence on potassium loading at the same carbon monoxide conversions. The water partial pressure may be viewed as depending primarily on kinetic factors at low CO conversion but as becoming dominated by equilibrium factors at high CO conversion.

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 (Eqs. [1] and [2]) dictates that

$$r_{\text{WGS}} \leq r_{\text{FTS}}. \quad [8]$$

Hence, a more reliable measure of the extent of the WGS reaction is how closely the rate of the WGS approaches that of the FTS. As shown in Fig. 7, the ratio of the WGS rate to the FTS reaction rate increases with carbon monoxide conversion and approaches a value of one.

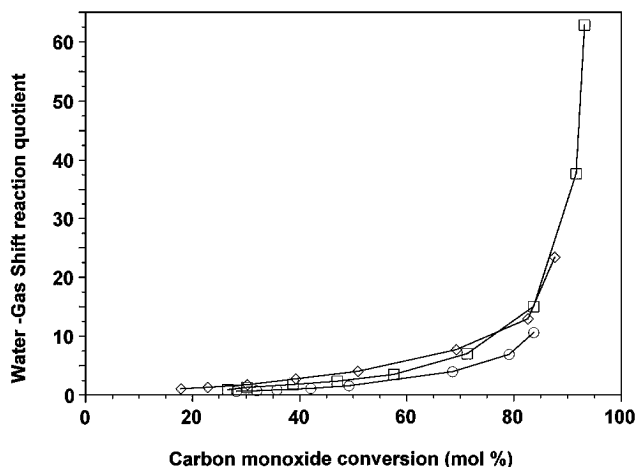


FIG. 6. Water-gas shift reaction quotient as a function of carbon monoxide conversion.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

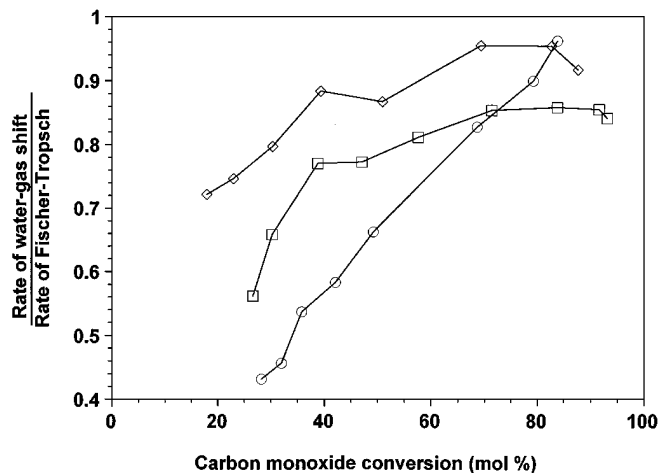


FIG. 7. Ratio of rate of water-gas shift to rate of Fischer-Tropsch synthesis reaction as a function of carbon monoxide conversion.  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

### Kinetics

The reaction rate expression given in Eq. [3] can be linearized by rearrangement as

$$\frac{P_{H_2}}{-r_{CO-H_2}} = \frac{1}{k} + \frac{b}{k} \frac{P_{H_2O}}{P_{CO}P_{H_2}}. \quad [9]$$

Hence a plot of  $P_{H_2}/-r_{CO+H_2}$  versus  $P_{H_2O}/P_{CO}P_{H_2}$  should give a straight line with intercept of  $1/k$  and slope of  $b/k$ .

The data for the three potassium loadings studied are plotted in this manner in Fig. 8. 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 Fig. 8 have been drawn through the data obtained at low conversions. This situation is analyzed under Discussion.

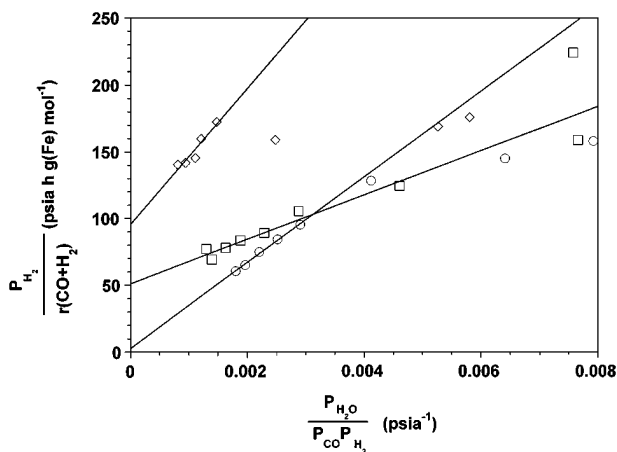


FIG. 8. Plots of the linearized version of Eq. [3].  $\circ$ , 0.36 K;  $\square$ , 1.4 K; and  $\diamond$ , 2.2 K.

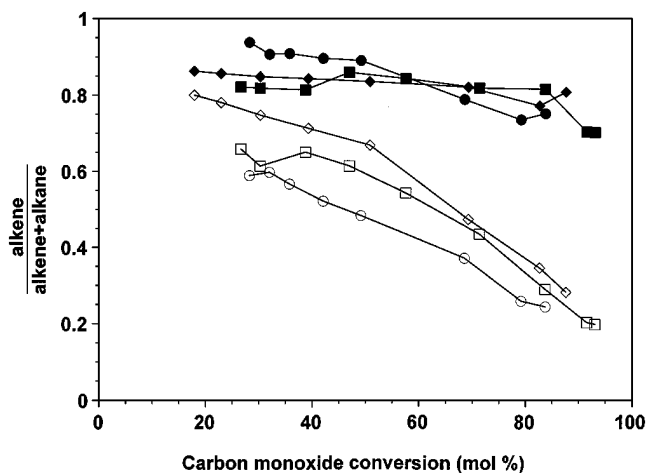


FIG. 9. Alkene selectivity of  $C_2$  (open symbols) and  $C_3$  (closed symbols) hydrocarbons as a function of carbon monoxide conversion.  $\circ$ ,  $C_2$ , 0.36 K;  $\bullet$ ,  $C_3$ , 0.36 K;  $\square$ ,  $C_2$ , 1.4 K;  $\blacksquare$ ,  $C_3$ , 1.4 K;  $\diamond$ ,  $C_2$ , 2.2 K; and  $\blacklozenge$ ,  $C_3$ , 2.2 K.

### Alkene Selectivity

Figure 9 illustrates the alkene selectivity of the light hydrocarbon products,  $C_2$  and  $C_3$ . There is a strong dependence on carbon number for alkene selectivity with the Fischer-Tropsch synthesis (9). Studies with  $^{14}C$ -labeled alkenes show that secondary hydrogenation reactions are a major factor with ethene and then decrease to be insignificant with  $C_4$ - $C_5$ -alkenes. In conformity with this, the  $C_3$ -alkene fraction shows little dependence on either CO conversion or on alkali content. For ethane, the alkene fraction depends on both alkali content and on CO conversion, with CO conversion having a greater impact than alkali content.

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. The selectivity to 1-butene decreases with increasing carbon monoxide conversion and increases with increasing potassium loading at similar carbon monoxide conversions (Fig. 10). Up to about 60% CO conversion, there is little dependence on CO conversion but there is dependence on potassium content. Above about 60% CO conversion, 1-butene content decreases rapidly and is more dependent on CO conversion than potassium content in the catalyst.

### Methane Selectivity

The methane selectivity was constant at 5–6% of hydrocarbons and was similar for all the catalysts studied at low carbon monoxide conversions. Above 50% carbon monoxide conversion, the methane selectivity increased slightly with increasing conversion; with increasing potassium content the methane fraction was slightly lower (Fig. 11).

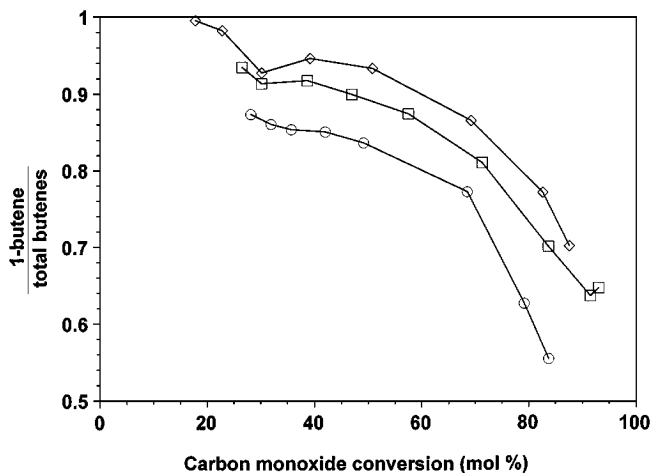


FIG. 10. Fraction of 1-butene in total linear alkenes as a function of carbon monoxide conversion. ○, 0.36 K; □, 1.4 K; and ◇, 2.2 K.

## 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 Eqs. [1] and [2] the maximum carbon monoxide conversion would be 31%, assuming  $H_2/CO = 0.67$  and  $n = 2.3$  (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. The rate of hydrogen consumed by the FTS reaction can be calculated from the stoichiometry of the FTS (Eq. [1]) as

$$H_2 \text{ consumed by FTS} = r_{FTS}(1 + (n/2)). \quad [10]$$

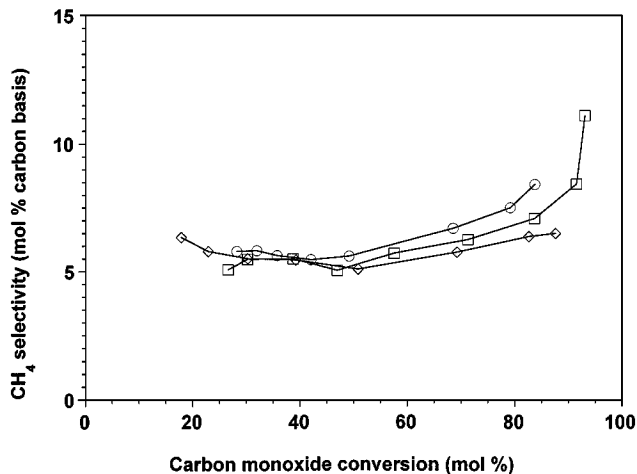


FIG. 11. Methane selectivity as a function of carbon monoxide conversion. ○, 0.36 K; □, 1.4 K; and ◇, 2.2 K.

At low carbon monoxide conversions or reaction times the extent/rate of the WGS reaction is not critical. The amount of hydrogen supplied to the reactor is sufficient for the FTS. At these conversion levels, the only determinant of the overall FTS activity is the FTS reaction (Eq. [1]). As shown in Figs. 1 and 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 rate 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 (Eq. [1]) but also by the WGS reaction (Eq. [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 (Eq. [1]) and the WGS reaction (Eq. [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 (Fig. 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 Fig. 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 (Fig. 2). According to this explanation, potassium actually inhibits the rate of the FTS reaction (Eq. [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 Eq. [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 Fig. 3 or 4 with Fig. 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

The data clearly show that the FTS reaction must depend increasingly on the hydrogen formed by the WGS reaction as the reaction time or the 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 (Eq. [1] or Eq. [2]) with carbon monoxide conversion. This provides an explanation for the nonlinearity of the experimental results when they are plotted (Fig. 8) according to the linearized version of Eq. [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 Fig. 8 for the data at carbon monoxide conversions below 60%. Information obtained from these regression lines then correspond primarily to the FTS reaction (Eq. [1]) and not to the WGS reaction (Eq. [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 Fig. 12. This decrease in the rate constant is more than an order of magnitude between loadings of 0.36 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 (Eq. [1]).

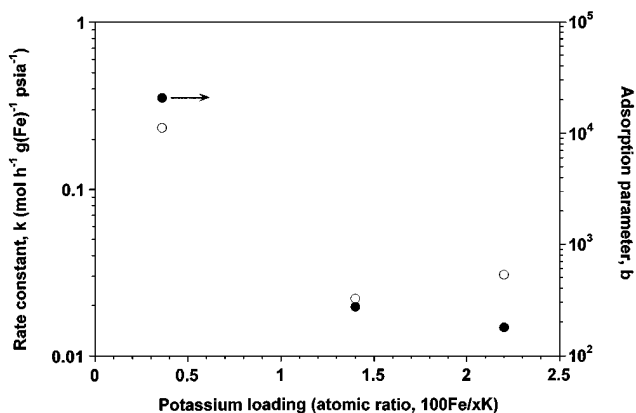


FIG. 12. Fischer-Tropsch rate constant,  $k$  (○), and adsorption parameter,  $b$  (●), as a function of potassium loading.

The adsorption parameter ( $b$ ) also decreases with potassium loading as shown in Fig. 12. Similar to the extent of decrease in the rate constant, the adsorption parameter decreases by over an order of magnitude between 0.36 and 2.2 K loadings. The adsorption parameter has been shown to be given by (5)

$$b = \frac{K_{\text{H}_2\text{O}}}{K_{\text{CO}}}, \quad [11]$$

where  $K_{\text{H}_2\text{O}}$  and  $K_{\text{CO}}$  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, 10, 11) 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

The amount of potassium as well as the level of CO conversion may impact selectivity. For the production of methane the potassium level has little, if any, impact up to about 50% CO conversion and above this level increasing potassium content slightly decreases the amount of methane that is produced. Neither potassium loading nor CO conversion significantly impact the fraction of propene in the C<sub>3</sub> products. For ethene selectivity, increasing potassium loading increases the amount of alkene but CO conversion has a larger impact. The fraction of 1-butene in the butene products increases with increasing potassium; however, above about 50% CO conversion levels the potassium loading is less important than CO conversion.

### 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 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 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.

In contrast to previous studies, the effects of potassium on catalyst selectivity have been compared at similar con-

versions. 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.

#### ACKNOWLEDGMENT

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