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Silica-Supported Iron Nitride in Fischer–Tropsch Reactions

II. Comparison of the Promotion Effects of Potassium and Nitrogen on Activity and Selectivity

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The performance of silica-supported iron catalysts promoted by potassium and nitrogen has been studied for the conversion of CO to hydrocarbons. Reactions were investigated at 250°C and at 1, 7.8, and 14 atm in a differential conversion range of less than 6%. Significant differences exist in the behavior of these supported catalysts in comparison to prior studies of fused or precipitated materials. It was found that an unpromoted Fe-carbide catalyst was more active at lower pressures and less active at higher pressures than the nitrided catalyst. Moreover, it was found that potassium-promoted catalysts were less active than catalysts without potassium. Both Fe-nitride and potassium-promoted catalysts showed higher olefin selectivities, higher water–gas shift activity, lower alcohol yields, and larger proportions of higher molecular weight products than their unpromoted counterparts. The product distribution parameters are presented for all catalysts at different pressures and conversion levels. The significance of the incorporation of alcohols into the distribution plot is discussed and a mechanism for alcohol formation is proposed. The effect of nitrogen on the catalytic reaction is discussed in terms of a donor model theory in which nitrogen atoms donate electrons to the iron *d* band. From the product distribution of the supported Fe-nitride and potassium-promoted catalysts, it is concluded that nitrogen and potassium have a similar promoting function on the Fischer–Tropsch reactions and further that an additive effect is observed for Fe-K-nitride catalysts.

INTRODUCTION

In the previous paper (*1*), the composition of the silica-supported Fe-nitride catalyst was studied by the methods of Mössbauer effect spectroscopy and X-ray diffraction analysis. This paper presents activity/selectivity results for both potassium- and nitrogen-promoted supported iron catalysts in the syngas reaction. A distinction was made in the prior paper between Fe-carbide and Fe-nitride depending upon whether the reduced catalysts had gone through the nitridation process before reaction or not. In this paper, potassium-promoted iron catalysts are also designated in a similar manner, namely Fe-K-carbide and Fe-K-nitride.

Potassium has been used as a promoter for various types of catalysts for many years. In applications to iron catalysts used for synthesis reaction it has been proposed that potassium atoms donate electrons to iron thus weakening the C–O bond when carbon monoxide attaches to an iron surface (*2*). About 1950, the Bureau of Mines initiated studies of iron nitride catalysts in Fischer–Tropsch reactions. Those materials were initially either fused or precipitated magentite with other components such as MgO, CuO, Al_2O_3, and K_2O as promoters. In this study, iron nitrides supported on silica were prepared with or without potassium for purposes of direct comparison.

Reaction rates are expressed as turnover numbers, with the number of sites based upon the hydrogen chemisorption of the reduced metal (*3*). All activity and selectivity determinations, as well as water–gas shift

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activity, were measured as a function of percentage of CO converted into hydrocarbons ($C_1 \sim C_9$) and alcohols (methanol and ethanol). Product distributions are presented and characterized by the chain growth parameter.

The yield of product i, Y_i, with respect to reactant j is defined as the ratio of moles of j converted to i to the moles of j initially present, namely,

$$Y_i = \frac{\text{moles of } j \text{ to } i}{\text{moles of } j \text{ initially present}}.$$

The mole fraction of product i, P_i, is based on 1 mol of feed gas that produces x_i moles of product i. Thus

$$P_i = \frac{x_i}{F_{\text{out}}},$$

where F_{out} is the total moles of effluent per mole of reactants fed (H_2 + CO).

Selectivity in this study is defined as the ratio of product turnover numbers for two components; water–gas shift activity is defined as the ratio of the mole fraction of CO_2 to that of water (*3*).

EXPERIMENTAL

1. Catalyst Preparation

The preparation of potassium-free catalysts (Fe-carbide and Fe-nitride) has been described in the preceding paper (*1*). In the case of potassium-promoted catalysts, potassium carbonate was coimpregnated with iron nitrate solution onto Davison 62 silica gel. The iron loading is 9.9% based on iron metal and the K : Fe molar ratio is 0.0175. The thermal treatments are similar to those described in (*1*).

2. Synthesis Experiments

The medium-pressure, single-pass, fixed-bed reactor system used is depicted in Fig. 1. Details of construction and operation have been reported by Amelse *et al.* (*3*) and Arcuri *et al.* (*7*). Catalysts were first reduced at 425°C for 24 h in hydrogen. For nitride preparation they were then switched to NH_3, the temperature raised to 495°C for 12 h and the samples subsequently cooled to room temperature in NH_3. For the carbided catalyst, samples were cooled in H_2 after reduction, prior to conducting the CO/H_2 synthesis reactions at 250 ± 2°C. The reactants were obtained from Airco Industrial Gases as premixed mixtures (CO : H_2 is either 1 : 1 or 1 : 3) in aluminum cylinders in order to reduce carbonyl formation. However, low levels of carbonyl were observed so a 5-Å-sieve cold trap was employed in the feed system. Minimal purity for CO is 99.3% and for H_2 is 99.999%. Oxygen removal was provided by a MnO_2/SiO_2 trap prereduced in flowing H_2 at 350° for about 1 h. This trap serves as its own indicator, turning from a blue–green in the reduced state to brown–black as it oxidizes. Details

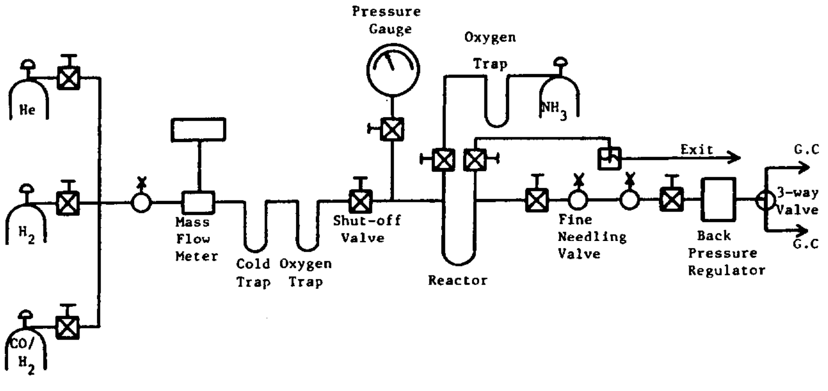

FIG. 1. Experimental system for activity and selectivity measurements.

of the chromatographic calibration and product separation are described elsewhere (*4*). All turnover frequencies are based on a surface area measurement determined from the amount of hydrogen chemisorbed during the flow-desorption experiment developed by Amelse (*3*, *6*). Hydrogen is chemisorbed as the temperature is decreased from 450 to 0°C, reversibly adsorbed H_2 removed by flushing in Ar at 25°C, and a measure of the chemisorbed H_2 taken as that desorbed on temperature programming from 25 to 450°C.

RESULTS

1. Rate Data as a Function of Percentage CO Conversion

Although there can be many products in a typical Fischer–Tropsch reaction, in this work analysis was conducted for hydrocarbons up to C_9 plus methanol and ethanol. The term "percentage CO conversion" refers specifically to the conversion of CO to these products and does not include CO consumed in forming CO_2. All rate data were obtained at 250°C and at steady-state conditions, namely, the catalyst state and product distribution are constant with respect to time in the flow reactor system.

Figure 2A is the time scale of turnover frequency (N_{CO}) of Fe-carbide and Fe-K-carbide at a fixed gas hourly space velocity (GHSV) at 7.8 atm with 1/3 (CO : H_2) feed gas. Deactivation seems to be negligible. The stabilities of Fe-nitride and Fe-K-nitride at 7.8 atm with 1/3 feed are shown in Fig. 2B. It is seen that N_{CO} is quite stable up ca. 50 h; however, when the ethylene and propylene selectivities (represented by $N_{C_2^=}/N_{C_2}$ and $N_{C_3^=}/N_{C_3}$, respectively, and discussed in next section) at a fixed GHSV are plotted with respect to time (Figs. 3A and B) there is an initial decrease up to 25 h (Fe-nitride), then the selectivities level off with respect to time. The similar shape of both ethylene and propylene selectivities and equivalent times (~25 h) for equilibration provide reasonable evidence that the Fe-nitride catalyst is at steady state after 25 h of reaction. However, considering the GC accuracy vis-à-vis relatively small changes in the selectivity of ethylene and propylene one may realize that, after 15 h, these changes (5.5 and 2%, respectively) are within the limits of the accuracy of analysis (±6%) and thus both Fe-nitride as well as Fe-K-nitride catalysts are regarded as reaching their "steady states" after 15 h of reaction. Rather extensive deactivation has been reported for Fe_4N (*5*) under similar conditions. For the carbided catalyst, steady state is observed within 1 h, after which the reduced iron is fully carburized in the syngas atmosphere (*6*).

Listed in Table 1 are the CO turnover numbers, N_{CO}, for Fe-carbide and Fe-ni-

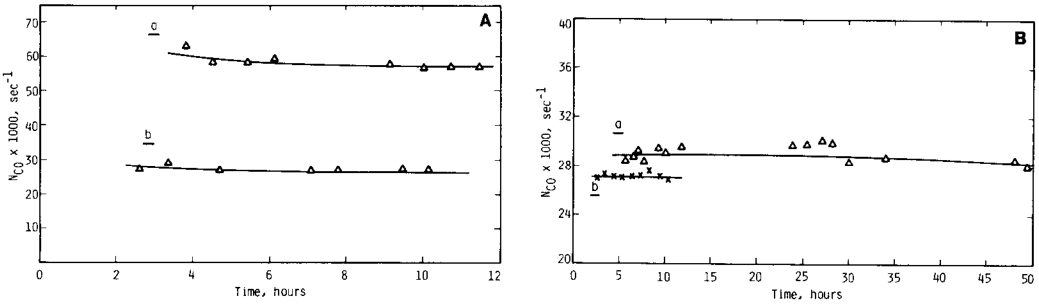

FIG. 2. (A) CO turnover frequency as a function of time for 1/3 feed: (a) Fe-carbide, 7.8 atm, GHSV = 600, 7.2% conversion. (b) Fe-K-carbide, 7.8 atm, GHSV = 264, 6.5% conversion. (B) CO turnover frequency as a function of time for 1/3 feed: (a) Fe-nitride, 7.8 atm, GHSV = 255, 8.5% conversion. (b) Fe-K-nitride, 7.8 atm, GHSV = 240, 7.6% conversion.

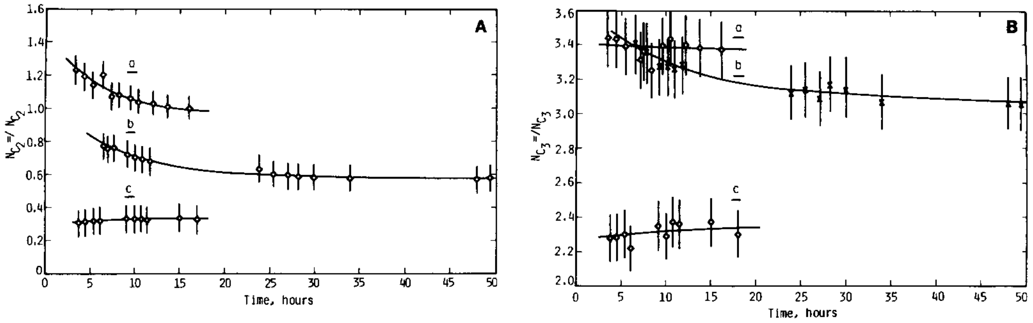

FIG. 3. (A) Ethylene selectivity as a function of time for 1/3 feed at 7. 8 atm: (a) Fe-K-nitride, GHSV = 240, 7.6% conversion. (b) Fe-nitride, GHSV = 255, 8.5% conversion. (c) Fe-carbide, GHSV = 255, 8.7% conversion. (B) Propylene selectivity as a function of time for 1/3 feed at 7.8 atm: (a), (b), (c) as in (A).

tride catalysts at 3 different pressures for both 1/1 and 1/3 CO/H_2 feed gas mixtures (at 2% CO conversion). N_{CO} values increase as the pressure changes from 1 to 7.8 atm, but there is no further increase in N_{CO} as pressure goes up from 7.8 to 14 atm except for the nitrided catalyst with 1/3 feed mixture. In all cases, N_{CO} decreases with increasing conversion as is shown in Fig. 4 for the Fe-carbide catalyst. The decrease in activity with increasing conversion has also been reported elsewhere (*6*, *7*) and is attributed either to some type of product inhibition or to slower CO consumption rates as hydrocarbon chains grow. In all reactions with the 1/3 feed mixture for both carbide and nitride catalysts there seems to be no deactivation during the course of an experiment. With the 1/1 feed mixture however, there is about a 10% decrease in CO turnover number after 15 h at all pressures investigated. This deactivation is very probably due to carbon deposition which causes surface-active site fouling (*8*).

The CO turnover numbers for carbide and nitride catalysts are about the same at 1 atm. However, carbide and nitride catalysts behave quite differently at higher pressures: the nitride catalyst is more active with 1/1 feed gas at both 7.8 and 14 atm and with 1/3 feed gas at 14 atm, whereas the

TABLE 1

CO Turnover Frequencies (N_{CO}) of Fe-Carbide and Fe-Nitride at Various Pressures and Feeds at 250°C (2% CO Conversion) (×10^3 molecules/site-sec)

Catalyst:	Fe-Carbide		Fe-Nitride	
Feed gas CO/H_2 ratio:	1/3	1/1	1/3	1/1
Pressure (atm)				
1	15 ± 2	6.1 ± 0.1	11 ± 0.2	5 ± 0.1
7.8	74 ± 4	26.0 ± 0.4	40 ± 3	37 ± 2
14	63 ± 5	24.5 ± 0.5	97 ± 6	43 ± 2

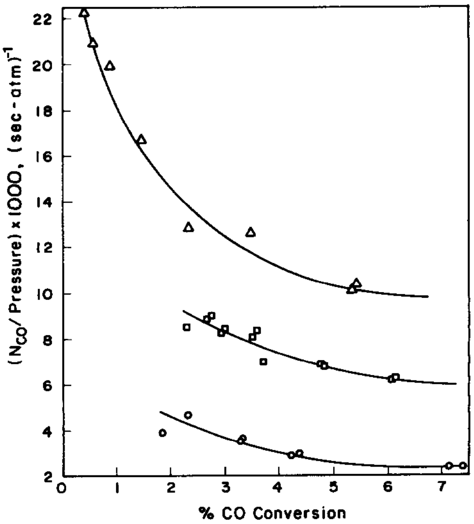

FIG. 4. CO turnover frequency vs conversion as a function of pressure for 1/3 feed; △ = 1 atm, □ = 7.8 atm, ○ = 14 atm.

TABLE 2

CO Turnover Frequencies (N_{CO}) of Fe-K-Carbide and Fe-K-Nitride at Various Pressures and Feeds at 250°C (2% CO Conversion) ($\times 10^3$ molecules/site-sec)

Catalyst:	Fe-K-Carbide		Fe-K-Nitride	
Feed gas CO/H_2 ratio:	1/3	1/1	1/3	1/1
Pressure (atm)				
1	11.0 ± 0.3	2.3 ± 0.2	12.0 ± 0.3	3.2 ± 0.2
7.8	23.4 ± 1.5	9.4 ± 0.8	29.3 ± 1.5	15.6 ± 1.5
14	46.2 ± 2.5	14.0 ± 1.2	39.2 ± 2.5	28.7 ± 1.5

carbide catalyst is more active with 1/3 feed gas at 7.8 atm. Earlier studies by Anderson and co-workers (*9, 10*) also indicated that nitrided iron catalysts were more active with 1/1 feed gas at 7.8 atm.

For the potassium-promoted Fe-K-carbide and Fe-K-nitride catalysts, the N_{CO} values at 2% CO conversion are listed in Table 2. These N_{CO} values increase as the pressure increases. However, all values are smaller than for the potassium-free catalysts. Fe-K-nitride seems to be more active than Fe-K-carbide except for the case of 1/3 feed gas at 14 atm. N_{CO} values drop as the % CO conversion increases, in a manner similar to that of the potassium-free catalyst.

2. *Ethylene and Propylene Selectivities*

The conversion dependence of the steady-state $N_{C_2^=}/N_{C_2}$ ratio for Fe-carbide and Fe-nitride catalysts at 14 atm is shown in Fig. 5A for the 1/3 feed gas mixture. The general trend shown for the steady-state $N_{C_2^=}/N_{C_2}$ ratio is the same at 1 and 7.8 atm, decreasing with increasing conversion, consistent with the view that the initial products are olefins. In all cases studied, the Fe-nitride catalyst gives a $N_{C_2^=}/N_{C_2}$ ratio which is more than twice that of Fe-carbide. Note especially the first two samples in Fig. 5A, denoted O_1 and O_2, which were taken early in the experiment and which have a selectivity ratio about 6 times larger than that for Fe-carbide catalyst.

It has been claimed that a potassium-promoted iron catalyst will give higher olefin ratios (*2*). In Fig. 5B, it is seen that the $N_{C_2^=}/N_{C_2}$ values increase slightly with pressure for the Fe-K-carbide catalyst. Com-

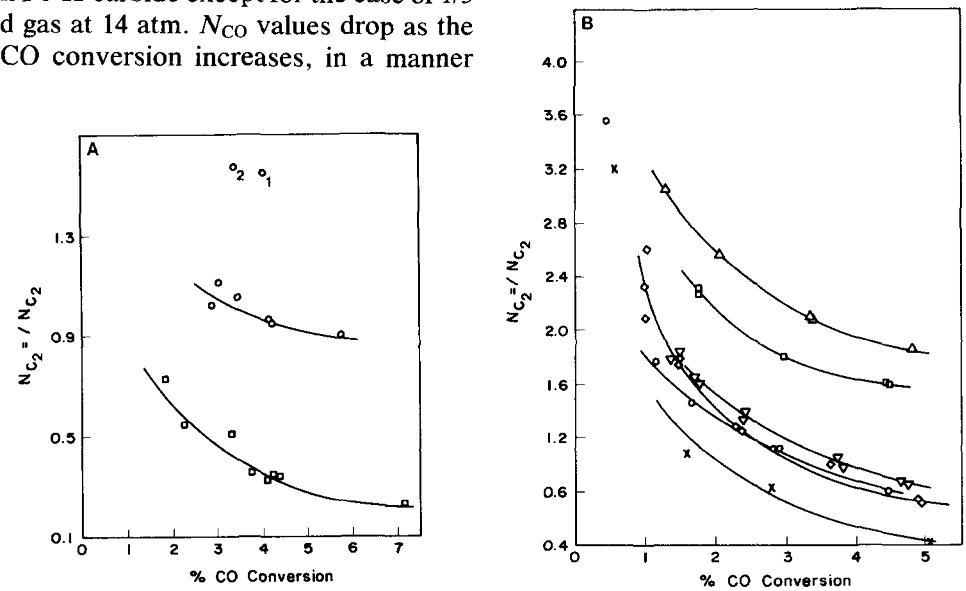

FIG. 5. (A) Ethylene selectivities vs conversion for 1/3 feed at 14 atm; O = Fe-nitride (O_1 and O_2 were measured after 18 and 64 min of reaction, respectively); □ = Fe-carbide. (B) Ethylene selectivities vs conversion for 1/3 feed at different pressures; ○, ◇, ▽ = Fe-K-carbide at 1, 7.8, and 14 atm; ×, △, □ = Fe-K-nitride at 1, 7.8, and 14 atm.

pared with the unpromoted material, the Fe-K-carbide catalyst boosts the $N_{C_2^=}/N_{C_2}$ value from 0.5 to 1.1 at about 3% CO conversion. On the other hand, the Fe-K-nitride catalyst shows a very strong pressure dependence for ethylene selectivities. At 1 atm, the $N_{C_2^=}/N_{C_2}$ value for Fe-K-nitride is smaller than for the Fe-K-carbide, but as the pressure increases the value increases from about 0.7 to 2.1 at 3% conversion. Fe-K-nitride shows the highest ethylene selectivity of all four catalysts studied. The same type of behavior is observed for the $N_{C_3^=}/N_{C_3}$ ratio, although for a given conversion, the fraction of $C_3^=$ olefins is greater. Thus, the promotion effect of potassium on olefin selectivity is well supported by these results.

3. Relative Activities for Alcohols

At 1 atm alcohol production from iron-based Fischer–Tropsch catalysts is very small. However, at higher pressures alcohols become substantial products. Figure 6a depicts the mole fraction of methanol produced by Fe-carbide and Fe-nitride; with the 1/1 mixture at 7.8 atm the carbide catalyst produces about twice the amount of methanol compared with the nitride catalyst. A similar relationship exists for the ethanol mole fraction, with the iron carbide producing more ethanol than the iron nitride.

The total C_1 + C_2 alcohol mole fraction vs % CO conversion for potassium-promoted catalysts is plotted in Fig. 6b. On comparison of Figs. 6a and b it would appear that potassium-promoted catalysts retard methanol selectivity. However, with the copresence of potassium and nitrogen, Fe-K-nitride produces more methanol and ethanol (see Fig. 6b). Anderson and coworkers (*9*) claimed that with bulk nitrided iron catalyst (with K_2O as one of the ingredients) alcohol production was greatly enhanced. The present results are consistent.

Although the alcohol mole fraction is the scale used to measure the selectivity of alcohol production, the absolute activity for alcohol formation is expressed in terms of its yield. Figures 7a and b show that both Fe-carbide and Fe-K-carbide yield more alcohol (methanol and ethanol) than their nitrided counterparts at 14 atm with the 1/1 mixture. However, with the 1/3 mixture, Fe-K-carbide and Fe-K-nitride produce about the same amount of alcohol, as shown in Fig. 7c.

It can be concluded that in general the Fe-carbide catalyst produces more alcohol than Fe-nitride and Fe-K-carbide or Fe-K-nitride. Comparison of the two potassium-promoted catalysts reveals essentially equivalent yields of alcohol.

4. Water–Gas Shift Activity

Although feed mixtures of CO/H_2 with ratios of 1/1 and 1/3 were used throughout

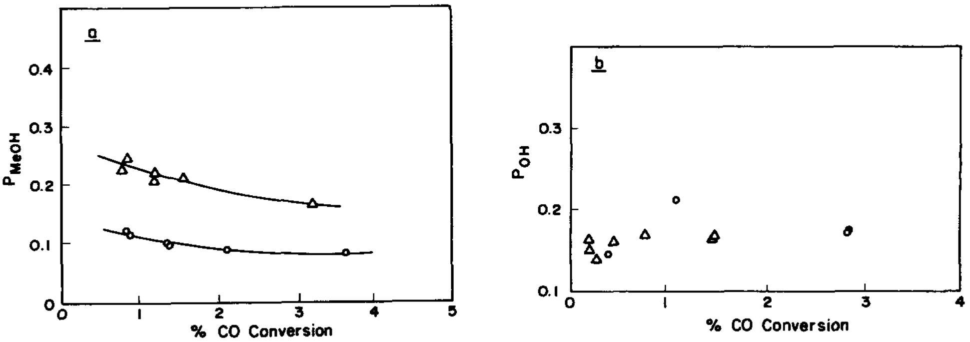

FIG. 6. (A) Methanol mole fraction vs CO conversion for 1/1 feed at 7.8 atm: △ = Fe-carbide; ○ = Fe-nitride. (B) Total C_1 + C_2 alcohol mole fraction vs CO conversion for 1/1 feed at 7.8 atm: △ = Fe-K-carbide, ○ = Fe-K-nitride.

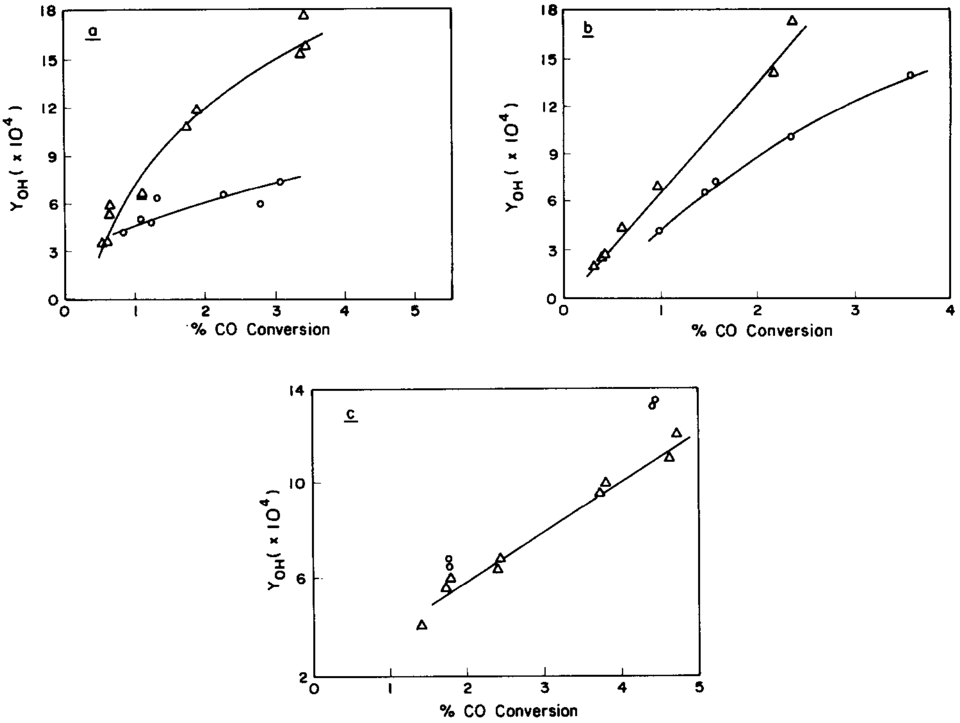

FIG. 7. Total alcohol yield vs CO conversion for 1/1 feed at 14 atm; (a) △ = Fe-carbide, ○ = Fe-nitride; (b) △ = Fe-K-carbide, ○ = Fe-K-nitride; (c) yields for 1/3 feed at 14 atm; △ = Fe-K-carbide, ○ = Fe-K nitride.

the study, the actual reaction mixture compositions are modified by the presence of the water–gas shift reaction shown below, which occurs concurrently with the synthesis reactions on the catalyst surface:

$$CO + H_2O \rightleftarrows CO_2 + H_2;$$

$$K = \frac{P_{H_2}P_{CO_2}}{P_{H_2O}P_{CO}}. \quad (1)$$

This is a thermodynamically reversible reaction with equilibrium constant increasing as the temperature is lowered. At 250°C, the equilibrium constant is about 83 (*11*). This reaction, although no hydrocarbon is produced, changes the internal hydrogen economy in a Fischer–Tropsch process. In the present study, where low conversion is maintained, the ratio X_{CO_2}/X_{H_2O}, with X the mole fraction of these nonhydrocarbon products, gives a measurement of the extent of forward reaction of Eq. (1), and we refer to it for convenience as "shift activity."

The mole fraction of CO_2 in the reactor effluent was measured directly by gas chromatography (*3*). However, since water gives a broad background peak in the GC separation, the rate of water formation was calculated by assuming that the hydrocarbon product distribution terminated at C_9 and alcohols terminated at C_2.[1] Since each molecule of H_2O that formed from the synthesis reaction may shift to CO_2, at steady state the molar rate of consumption of CO equals the sum of the molar rate of formation of H_2O and CO_2. The validity of such a calculation depends upon the fact that CO

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[1] An estimate of the error associated with this assumption can be made on the basis of the chain growth probability parameter, α, in Eq. (2). For $\alpha = 0.5$, the error in total hydrocarbons not accounted for is 1.2%, for $\alpha = 0.6$ it is 4.7%. Since α values here are typically of the order of 0.6, we estimate resultant maximum errors of 5%.

does not disproportionate to form carbon and CO_2. This is evidenced by stable turnover numbers during the period of reaction. Similar results with respect to disproportionation have been obtained by Amelse *et al.* (*3*) and Arcuri (*7*).

Figure 8A shows that Fe-nitride has higher shift activity than the Fe-carbide catalyst with 1/1 feed gas mixture, although the carbide and nitride catalysts exhibit similar activities at 1/3 feed gas ratio. However, with potassium-promoted catalysts, the nitrided catalyst has about the same shift activity as the carbided catalyst as is shown in Fig. 8B. More extensive comparison (not shown) of the shift activities of catalysts with and without potassium indicates that potassium-promoted catalysts show higher shift activities than potassium-free catalysts at all three pressures studied. Amelse, *et al.* (*3*) and Arakawa and Bell (*12*) have seen similar results with 1/3 mixtures. It should be noticed that in no case is the water–gas shift reaction near equilibrium. This can be seen from the fact that no X_{CO_2}/X_{H_2O} ratio is larger than 0.7, whereas the equilibrium value should be about 28 and 83 with the 1/3 and 1/1 gas mixtures, respectively, at 250°C.

5. Overall Product Distributions at Steady-State Conditions

5.1 Product chain length distribution. The chain growth probability parameter, α, is defined as the ratio of the rate of chain propagation to the sum of the rates of propagation and termination (*13*). Thus a larger α value indicates a higher probability to form larger molecules. There are several mathematical forms for the product distribution. The one used for the present analysis of α values is given as

$$\ln(y_i \times 10^6) = n \ln \alpha + b, \qquad (2)$$

where y_i is the sum of the product mole fractions that have i carbon atoms, n is the degree of oligomerization, or the carbon number in a chain, b is the Y-axis intercept, and α is the chain growth probability. The multiplication of y_i by 10^6 in Eq. (2) is used

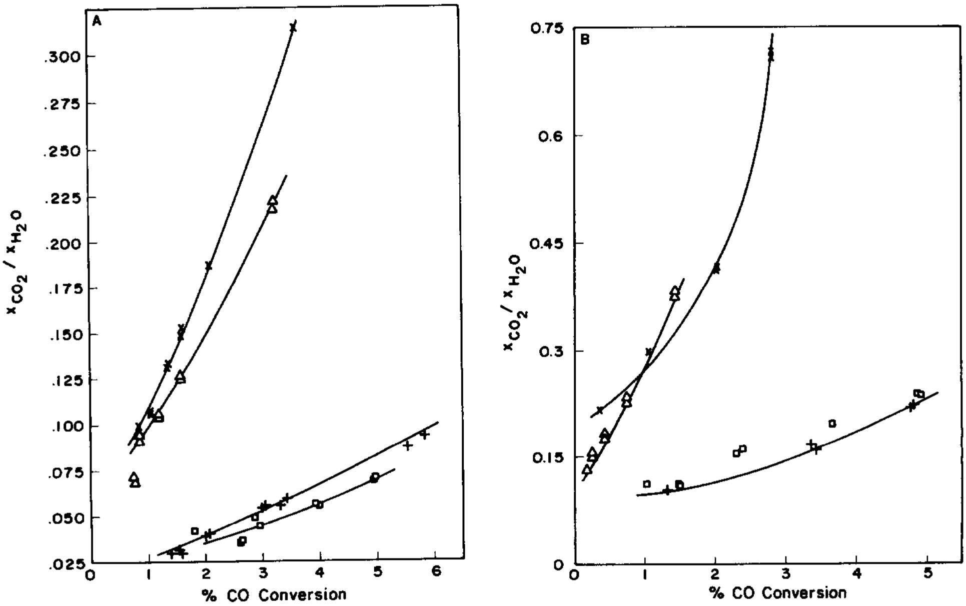


FIG. 8. Shift activities vs CO conversion at 7.8 atm: (A) × = Fe-nitride (1/1 feed); △ = Fe-carbide (1/1 feed); + = Fe-nitride (1/3 feed); □ = Fe-carbide (1/3 feed). (B) × = Fe-K-nitride (1/1 feed); △ = Fe-K-carbide (1/1 feed); + = Fe-K-nitride (1/3 feed); □ = Fe-K-carbide (1/3 feed).

for convenience to transform the logarithmic values to positive numbers. The y_i values include the C_1 and C_2 alcohols as will be explained in the discussion section. Figure 9 presents an example of typical results obtained.

The α values, calculated from the slope of the product distribution plots for Fe-carbide and Fe-nitride are given in Table 3. A trend that values increase with increasing pressure as well as CO conversion level is obvious, indicating that higher pressure and CO conversion level favor long chain formation. The α values also increase as the hydrogen content in the feed gas decreases. The hydrogen-rich environment is believed to favor hydrogen incorporation (chain termination) instead of carbon incorporation (chain propagation). In all cases studied, the nitride catalyst has larger values than the corresponding carbide. This indicates that Fe-nitride catalyst tends to form larger molecules with less hydrogenation (enhanced olefin ratio).

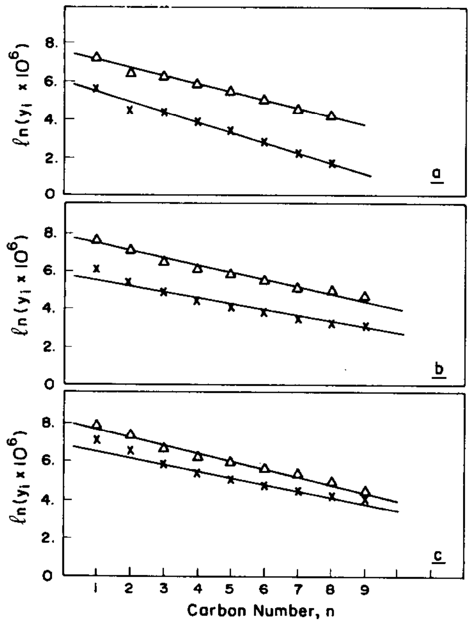


FIG. 9. A representative chain growth plot; Fe-K-nitride for 1/1 feed: (a) △ = 1.83% conversion; × = 0.26% conversion; 1 atm. (b) △ = 2.86% conversion; × = 0.57% conversion; 7.8 atm. (c) △ = 3.40% conversion; × = 1.58% conversion; 14 atm.

TABLE 3

Growth Parameters, α, for Fe-Carbide and Fe-Nitride Catalysts

Catalyst:	Fe-Carbide		Fe-Nitride	
Feed gas CO/H_2 ratio:	1/3	1/1	1/3	1/1
Pressure (atm)				
1	.554 (5.38)[a]	.607 (1.84)	.595 (3.91)	.619 (1.27)
	.521 (1.50)	.601 (0.84)	.525 (1.15)	.610 (0.25)
7.8	.597 (7.84)	.645 (3.25)	.651 (5.55)	.665 (3.66)
	.590 (2.93)	.638 (1.21)	.645 (2.05)	.654 (0.87)
14	.607 (7.14)	.650 (3.47)	.654 (7.23)	.670 (4.22)
	.590 (1.85)	.630 (1.11)	.649 (3.45)	.661 (1.06)

[a] Value in parentheses is % CO conversion.

The α values for the potassium-promoted carbide and nitride catalyst are listed in Table 4. Comparison among the α values of Table 3 indicates that potassium-promoted catalysts overall have larger α values. This is in agreement with prior results that these catalysts tend to form longer chain products (*2*). The previously described effects of feed gas composition, pressure and conversion level are also observed with the potassium-promoted catalysts. In all four catalysts studied, the Fe-K-nitride catalyst seems to have the highest α values, indicating an additivity of the effects due to potassium and nitrogen is observed in the overall product distribution.

TABLE 4

Growth Parameters, α, for Fe-K-Carbide and Fe-K-Nitride Catalysts

Catalyst:	Fe-K-Carbide		Fe-K-Nitride	
Feed gas CO/H_2 ratio:	1/3	1/1	1/3	1/1
Pressure (atm)				
1	.578 (4.47)[a]	.636 (1.32)	.637 (5.02)	.666 (1.83)
	.497 (1.68)	.607 (0.54)	.587 (1.61)	.587 (.264)
7.8	.620 (4.90)	.629 (1.49)	.694 (4.83)	.723 (2.86)
	.590 (1.51)	.620 (0.77)	.684 (1.95)	.686 (0.57)
14	.621 (4.65)	.654 (2.39)	.699 (4.49)	.736 (3.4)
	.613 (1.41)	.634 (0.98)	.682 (2.85)	.691 (1.58)

[a] Value in parentheses is % CO conversion.

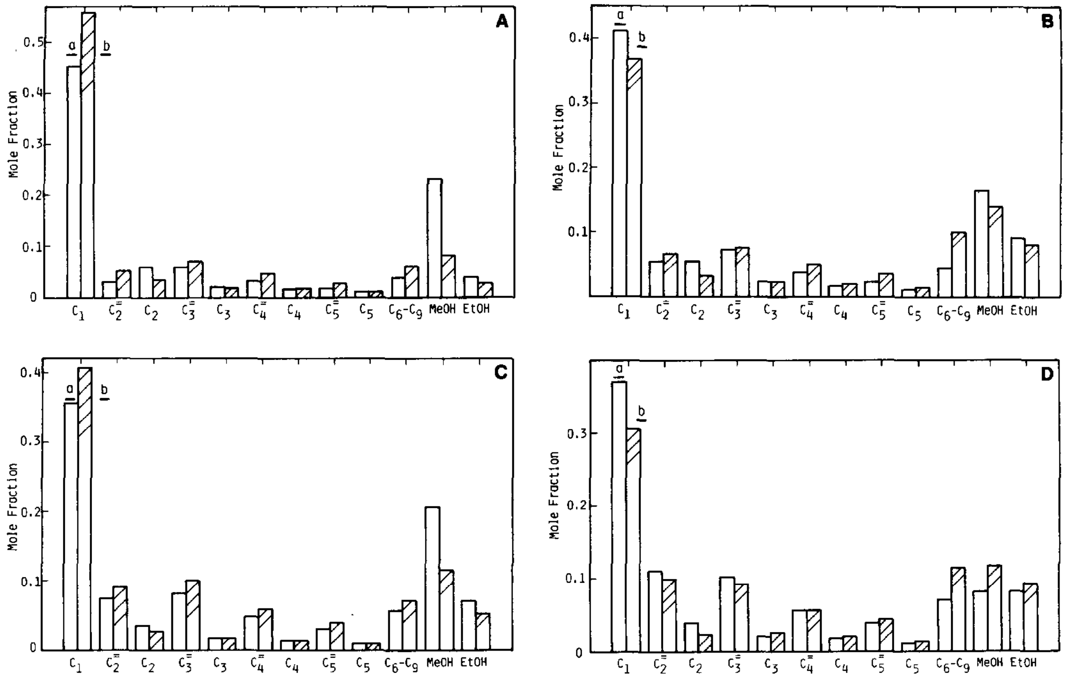


FIG. 10. Product distributions at 7.8 atm for 1/3 feed: (A) (a) Fe-carbide, 3.0% conversion; (b) Fe-nitride, 3.0% conversion. (B) (a) Fe-K-carbide, 3.66% conversion; (b) Fe-K-nitride, 3.38% conversion. Product distributions at 7.8 atm for 1/1 feed: (C) (a) Fe-carbide, 1.2% conversion; (b) Fe-nitride, 1.1% conversion. (D) (a) Fe-K-carbide, 1.49% conversion; (b) Fe-K-nitride, 1.09% conversion.

5.2 Total product distribution. The steady-state product distribution for any of the catalysts is a strong function of temperature, pressure, feed gas mixture ratio, and conversion range studied. Figures 10A to D present some examples of the total product distributions obtained at 250°C. The fact that the Fe-nitride catalyst produces more olefins, more $C_6 \sim C_9$ fractions and less alcohols than Fe-carbide is obvious. Potassium-promoted Fe-K-carbide also increases the olefin selectivity and $C_6 \sim C_9$ fractions of hydrocarbons, but decreases the alcohol production.

DISCUSSION

In the present paper the synthesis reaction results have been presented for the four catalysts investigated in order to compare the effects due to potassium and nitrogen. A summary of the observations for the reaction studies is listed below. In comparison with prior results on Fe/SiO_2 (*3, 7*), both the supported Fe-nitride and Fe-K-carbide catalysts have (1) higher olefin selectivity, (2) higher water–gas shift activity, (3) lower alcohol yield, (4) a tendency to shift products to larger molecular weight.

These tendencies are further enhanced for the Fe-K-nitride catalyst. Thus, from these observations on the behavior of both the K-promoted and nitrided catalysts, one may start to ponder the question of whether potassium and nitrogen are doing the same thing.

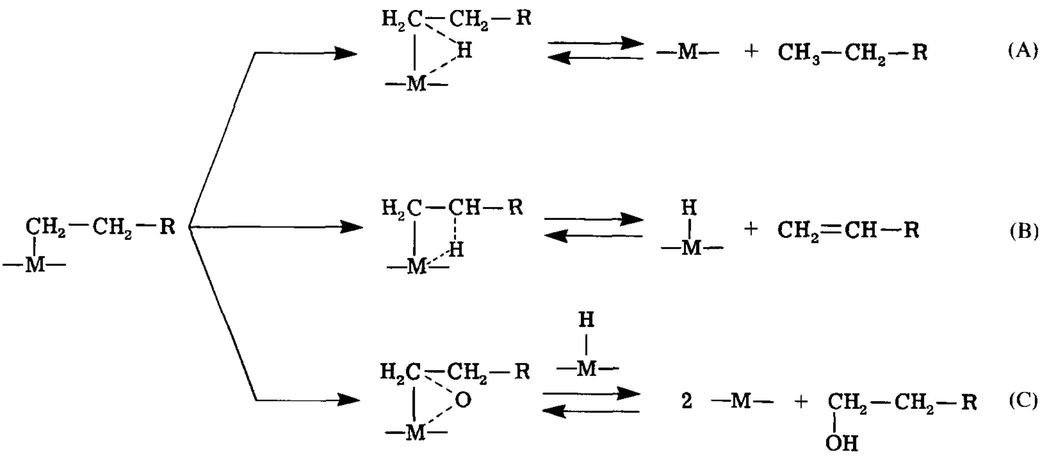
Potassium-promoted iron catalysts have been studied quite extensively (*2, 14, 15*) and the results indicate that potassium donates electrons to iron. Studies of iron nitride (*16–22, 27*) have shown that nitrogen also donates electrons to iron, in semiquantitative agreement with the "donor model" of Wiener and Berger (*23*).

The experimentally observed, approximately linear decrease of hyperfine field with the number of metalloid (C,N) neighbors (*21, 27, 28*) corresponds to a decrease of the iron magnetic moment by 0.52 μ_B for N neighbors and by 0.44 μ_B for C neighbors. This suggests that the charge-transfer into the partially filled iron 3*d* band is larger for interstitial nitrogen[2] than for interstitial carbon. The retention of about 15% interstitial N in the stabilized Fe-nitride catalyst (*1*) should therefore result in a slightly larger electron population in the iron *d* band as compared to the Fe-carbide.

Electron donation from potassium to iron has been indicated by earlier studies (*2, 14, 15*) for the K-promoted catalyst, but this was not seen in the Mössbauer spectrum of the reduced K-promoted catalyst. Probably, potassium atoms are segregated to the surface of the metal as has been proposed by Bonzel and Krebs (*29*). Alternately the electron donation could be in the 4*s* band, leaving the Fe-moment and the associated large core-polarization contribution to the hyperfine field unchanged. This should still change the conduction electron contribution, but this is usually a smaller effect in 3*d* metals (*31*). The discussion is beclouded by possible gradients in nitrogen content in the Fe-nitride catalyst. However, given the metallic properties of iron nitride, it is likely that the delocalized electron-enriched *d* band affects the catalytic behavior at the surface, leading to the similarity of behavior of nitrogen- and potassium-containing catalysts.

A final point has to do with the determination of y_i and resulting α values. The product distribution from Fischer–Tropsch reactions is an analog to that found for oligomerization reactions, and the calculation of y_i in Eq. (2) should include all products that derive from the same precursor. We believe there is evidence that alcohols as well as hydrocarbons involve the same intermediate. Figure 9 shows a typical example when alcohols are included in the product distribution plot. The linearity of the $n(y_2 \times 10^6)$ vs n plots seems to support this interpretation of the data.

Generalized product formation reactions can be written in a summary form, then, as



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[2] The electron donation from interstitial nitrogen is different from (but not inconsistent with) the case of chemisorbed nitrogen on an iron surface where it is believed to accept electrons from iron (*26*). This is understandable because the octahedral interstices in the ε-phase can accommodate, without lattice strain, a sphere of radius less than about 0.56 Å. The interstices are too small for atomic nitrogen with a radius of 0.74 Å (*24*) or the still larger N ion. The estimated effective radius of nitrogen in ε-Fe_xN of 0.68 Å (*25*) is consistent with the view that interstitial nitrogen (and by similar argument, carbon, too) donates electrons and exists in the structure as positively charged ions.

The possibility that alcohol is found via CO insertion is akin to findings on metals such as Rh that have less tendency to dissociate CO. Alcohol formation is favored at higher pressures. Arcuri's (*7*) study of iron-based catalysts found that the sum of the fraction of CO converted to CH_4 plus methanol is approximately constant regardless of the operating pressure. Similar results were found in the present study, further suggesting that methane and methanol may be derived from the same intermediate. If methanol decomposes at low pressures (~1 atm) on the iron surface, pathway C will not be favored and the precursor intermediate shifts to the formation of methane via pathway A.

The reaction sequence shown can also be applied to catalysts that produce very small amount of alcohols. For example, Co catalysts yield very small amounts of methanol even at high pressures and produce more CH_4 than either Fe and FeCo catalysts at all pressures (*7*). However, the sum of fractions of CO converted to CH_4 and CH_3OH is smaller at higher pressures than at 1 atm. This is no surprise when the chain growth probability, α, of Co is compared with that of iron. Co, with 1/1 feed gas, gives an α value of 0.86 whereas Fe has an α value of only 0.56. This "compensation" effect is also consistent with a common intermediate for chain propagation or termination which results in paraffin, olefin, or alcohol (and possibly other minor products).

Despite the apparent success in the interpretation of the distribution plot for y_i at higher pressures when alcohols are incorporated in the calculation, two points are still unresolved. First, is that in plots such as Fig. 9, at 1 atm y_{C2} is still underestimated due to decreased alcohol formation. Second, is that the observed y_{C1} is sometimes greater than predicted by the linear plot. One possible reason for these discrepancies, according to Biloen and Sachtler (*30*), is that a constant chain growth probability α does not exist for very small chains. The second possibility is that there are multiple pathways for the formation of C_1 and C_2 hydrocarbons and the secondary reactions that involve C_2 hydrocarbon are very pressure-dependent. Further data, particularly with regard to the effect of pressure, are required to resolve these questions.

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