

## V.2. Promoter Effect Research

### V.2.1. Fixed Bed Reactor Tests with Hydrogen Activated Catalysts

#### V.2.1.1. Literature Review

It is well known that the stronger bases of the Group IA metals, especially potassium, are essential promoters in iron catalysts for Fischer-Tropsch synthesis. They have a marked effect on both the activity and selectivity of iron catalysts. Other promoters and/or carriers (CuO, Group II metal oxides, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) are added mainly to facilitate iron reduction, stabilize a high metal surface area, improve the mechanical properties, or to modify the selectivity by a small amount, however their effects are usually small in comparison to that of potassium (Anderson, 1956; Dry, 1981).

The overall effects of potassium on the behavior of iron catalysts have been extensively investigated and are well established. Kölbel (1960) reported results of chemisorption measurements with CO and H<sub>2</sub> on reduced precipitated iron catalyst, and of changes in electrical resistance upon CO and H<sub>2</sub> chemisorption on evaporated iron films and foils. He found that potassium promotion increases CO chemisorption and decreases H<sub>2</sub> chemisorption. This was explained by the fact that potassium donates electrons to iron facilitating CO chemisorption, since CO tends to accept electrons from iron. On the other hand, hydrogen at higher surface coverages donates electrons to iron (electron affinity decreases upon H<sub>2</sub> chemisorption) and the presence of electron donating alkali would be expected to weaken the iron-hydrogen bond. The net result of potassium promotion is a strengthening of the Fe-C bond, and weakening of the C-O and Fe-H bonds. These findings have been confirmed in several subsequent studies on different types of iron surfaces (e.g., Dry et al., 1969; Benziger and Madix, 1980; Arakawa and Bell, 1983).

The effect of potassium on activity and product selectivity has been studied over a variety of iron based catalysts (e.g., Anderson et al., 1952; Anderson, 1956; Kölbel and Giehring 1963; Dry and Oosthuizen, 1968; Bonzel and Krebs, 1981; Dry, 1981; Arakawa and Bell, 1983; Dictor and Bell, 1986; Donnelly and Satterfield, 1989). General observations regarding the effect of potassium promotion on iron catalysts for the FT synthesis include: (1) increase in average molecular weight (chain length) of hydrocarbon products (i.e., decrease in production of methane and light gases); (2) increase in olefin selectivity; (3) increase in activity for the water-gas-shift (WGS) reaction; (4) increase in carbon deposition and catalyst deactivation rate; and (5) increase in FT activity at low potassium concentrations, followed by decrease at

higher levels of promotion.

Copper has been widely used as one of promoters for FT synthesis on iron catalysts, particularly in bubble column slurry reactors (Kölbel and Ralek, 1980; Deckwer et al., 1982; Kuo, 1985). Its function is to decrease the temperature required for reduction of iron oxides. While several studies have been made of the individual effect of potassium promotion on unsupported iron, only a few investigations have been reported for copper promotion of precipitated iron catalysts that contain no potassium.

Kölbel et al. (1951) observed increase in the overall activity at very low levels (ca. 0.1 wt%) of copper promotion, with no further effects at higher copper loadings. Wachs et al. (1984) reported that product distributions do not change appreciably when copper is incorporated into an iron catalyst for experiments in a differential fixed bed reactor (CO conversion less than 1%).

Although the qualitative effects of potassium promotion on catalyst activity and selectivity have been clearly established in the above studies, the data illustrating quantitative effects at conditions of industrial relevance (elevated pressure, CO rich feed gas, high reactant conversions, steady state operation in the absence of significant catalyst deactivation) are still lacking. The present study was undertaken to provide detailed information on (1) individual effects of potassium and copper promotion (singly promoted Fe/K and Fe/Cu catalysts), and (2) combined promotional effects of copper and potassium (doubly promoted Fe/Cu/K catalysts) on activity and product selectivity of precipitated iron catalysts for Fischer-Tropsch synthesis at process conditions representative of industrial practice. Particular attention was given to the effects of promoters, reaction temperature and gas space velocity on FT and WGS activity, hydrocarbon product distribution, and olefin and oxygenates selectivities as a function of carbon number.

#### V.2.1.2. Experimental Procedure

Typically, 3.5 g of the catalyst (3 cc) was diluted 1:8 by volume with glass beads of the same size range (30/60 mesh) and charged into the reactor. All catalysts were reduced with hydrogen at 220°C, 500 cc/min and atmospheric pressure for 8 hours.

Seven catalysts were employed in the present study: an unpromoted iron, copper promoted catalyst (100 Fe/3 Cu, in parts per weight), three potassium promoted catalysts (100 Fe/x K, where x=0.2, 0.5 and 1.0), and two doubly promoted catalysts (100 Fe/3 Cu/ 0.2 K or 0.5 K). Concentrations of promoters in the two doubly promoted catalysts were chosen to be the same

as those of the singly promoted catalysts, in order to study their combined effect and provide means of comparison with the singly promoted catalysts.

Following reduction, the flow was switched to helium and the bed was cooled down to 190°C. The system was then pressurized to 1.48 MPa, the helium flow was cut off, and synthesis gas ( $H_2:CO=1:1$ ) was introduced at a gas space velocity (SV) of 2 NI/g-cat.h. The bed temperature was gradually increased to 250°C over a period of 30 h. The first mass balance was conducted after additional 40 h on stream. Catalytic tests typically lasted about 170 h, during which time five mass balances were made. One of these balances was a repeat of the base set of conditions: 1.48 MPa, 2 NI/g-cat.h and either 235°C (100 Fe/1 K catalyst) or 250°C (for the other six catalysts), whereas others were conducted at different process conditions. The effect of reaction temperature (235, 250 and 265°C) was studied at SV=2 NI/g-cat.h, and the effect of gas flow rate (SV=2 and 4 NI/g-cat.h; or 1 NI/g-cat.h for the unpromoted catalyst) was studied at 250°C. Tests with the two doubly promoted catalysts had longer duration (about 460 h) and no balances were made at 265°C. Instead, several mass balances were made with  $H_2/CO=0.67$  feed gas at 250°C and 260°C, between about 150 and 400 h on stream. Results at these process conditions have been presented in Sections V.1.6 and V.1.7 of this report.

#### V.2.1.3. Results and Discussion

##### Activity and Stability of Catalysts

Effects of reaction temperature and time on stream at 250°C on FT activity, measured by ( $H_2+CO$ ) conversion, are shown in Figures V.2-1a and V.2-1b, respectively. ( $H_2+CO$ ) conversion increases with the addition of either copper or potassium, but copper has a more pronounced effect on catalyst activity than does potassium at all three reaction temperatures. The activity increases significantly with increasing potassium content up to 0.5 g of K per 100 g of iron, but beyond this promoter concentration the effect is small (0.5 K vs. 1K per 100Fe). A synergistic effect is observed with doubly promoted catalysts, which have higher activity than singly promoted catalysts. Also, activities of the two doubly promoted catalysts were similar at both, 235°C and 250°C, i.e., the activity was independent of potassium content of the catalyst. ( $H_2-CO$ ) conversion increases with increasing reaction temperature, as expected.

In several previous studies with iron catalysts (Anderson et al., 1952; Anderson, 1956; Kölbel 1960, Kölbel and Giehring, 1963; Dry, 1981), it was reported that the overall catalyst activity either increases with potassium promotion or it passes through a maximum as a function

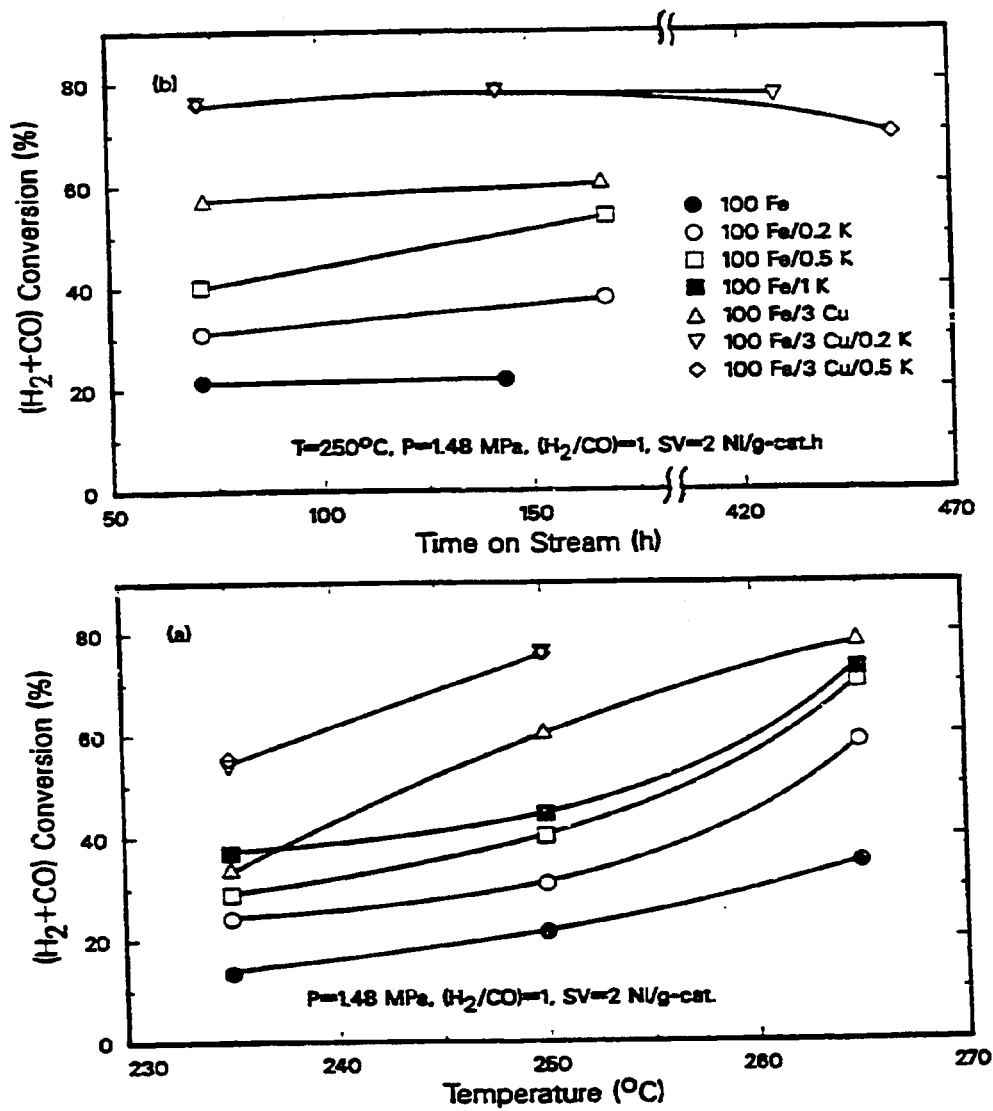


Figure V.2-1. Promoter effects on catalyst activity and stability, (a) (H<sub>2</sub>+CO) Conversion vs. reaction temperature, and (b) (H<sub>2</sub>+CO) Conversion vs. time on stream at 250°C.

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of potassium loading. On the other hand, Pichler (1952) reported that potassium in 0-5 wt%  $K_2CO_3$  range, had no effect on activity, whereas Arakawa and Bell (1983) and Dictor and Bell (1986) found that the activity of Fe/K catalysts was lower than that of the unpromoted catalyst. Arakawa and Bell employed an alumina supported catalyst containing 20% by weight of iron and K/Fe atomic ratios of 0.022-0.20. The latter ratios correspond to catalyst compositions of approximately 1.5-15 g of K per 100 g of Fe, and are significantly higher than those employed in previous studies including the present one. At the lowest potassium loading (100 Fe/1.5 K) the activity of the promoted catalyst was similar to that of the unpromoted catalyst. Lower activities were obtained at high potassium loadings which is consistent with results obtained in other studies. Dictor and Bell conducted experiments in a stirred tank slurry reactor at low CO conversions (less than 5%) with unpromoted hematite ( $Fe_2O_3$ ) powder, and potassium promoted  $Fe_2O_3$  (100 Fe/0.8 K). In this study, the catalysts were not activated prior to exposure to the synthesis gas ( $H_2/CO=3$ ) at 250°C and 8 atm, and it is possible that they had not reached their steady state activity.

The increase in catalyst activity with addition of potassium has been explained in terms of its structural and/or chemical promotional effects. Kölbel and co-workers (1960, 1963) made extensive characterization studies of catalysts with and without alkali, and found that potassium added in small amounts stabilizes surface area of the precipitated iron oxyhydrides and protects it against recrystallization during calcination. Reduced catalysts had maximum metal dispersion at potassium loadings of 0.15 and 0.3 wt%. The maxima in catalyst activity during synthesis were observed at these potassium loadings. Kölbel (1960) postulated that the reduced catalysts containing potassium had a much higher concentration of active sites than an unpromoted catalyst. At higher promoter concentrations, the active sites may be covered by potassium resulting in decline of the catalyst activity. Furthermore, increase in potassium fosters carbon deposition which blocks the active surface area leading to further decline in activity.

An alternative explanation for the promotional effect of alkali on the rate of FT was given by Dry and co-workers (Dry and Oosthuizen, 1968; Dry et al., 1969), who conducted studies on alkali promoted magnetite. They found that addition of alkali causes a decrease in surface area, which lead them to postulate that the promotional effect must be chemical in nature. As stated earlier, potassium promotion strengthens the metal-carbon bond, and weakens the carbon-oxygen bond. The latter facilitates removal of oxygen by hydrogen which is an essential

step in FT. According to Dry et al. (1969) the addition of alkali increases the rate of FT by increasing the rate of formation of the intermediate hydroxyl surface complexes.

The increase in activity with copper addition that was found in the present study, is in agreement with results obtained by Kölbel et al. (1951) at 230°C,  $H_2/CO=2$  and atmospheric pressure. Kölbel et al. observed an increase in overall activity at very low promoter levels (ca. 0.1 wt% of Cu), and further increases in the copper level had no additional effect. Deckwer et al. (1982) reported that 100 Fe/5.3 Cu catalyst had activity comparable to that of alkali promoted iron catalysts employed in previous studies of FT in slurry reactors, but they did not report any results for an unpromoted catalyst. The reasons for increased catalyst activity with the addition of copper are not clearly understood. It is known that copper facilitates reduction of iron, and that the total surface area of the catalyst decreases with the extent of metal reduction (Dry, 1981). This suggests that the higher activity of Fe/Cu catalysts relative to unpromoted iron may be attributed to differences in the size and number of  $\alpha$ -Fe and/or iron carbide crystallites during synthesis.

The effect of time on stream on FT activity at 250°C and 2 NI/g-cat.h is illustrated in Figure V.2-1b. The activity of all catalysts during the first mass balance at 250°C (72 hours on stream) was lower than the activity at 142-168 hours when the base conditions were repeated. The increase in activity was rather small, less than 5%, for the two doubly promoted catalysts, the unsupported iron catalyst and the 100 Fe/3 Cu catalyst. This means that these catalysts had achieved their steady state activity after about 40 hours at 250°C. However, catalysts promoted with potassium alone showed a marked increase in activity over the same period of time as shown in Figure V.2-1b (100 Fe/0.5 K) and Table V.2-1 (100 Fe/ 0.2 K). Also, ( $H_2-CO$ ) conversions, in tests with the 100 Fe/1 K catalyst at 235°C, were 23.5 and 37% at 48 and 168 hours on stream, respectively.

This increase in activity with time on stream is typical for hydrogen activated catalysts which are not reduced completely to zero valent state (Dry, 1981; Bukur et al. 1989). The catalyst activity increases during synthesis due to further reduction/carbiding which results in continued creation of active sites. Temperature programmed and isothermal reduction studies revealed that potassium inhibits reduction of iron when  $H_2$  is used as reductant, whereas copper facilitates the iron reduction even in the presence of potassium (Section VII). This explains the fact that the induction period during FT synthesis is much longer for Fe/K catalysts than with those containing copper.

The two doubly promoted catalysts were tested over a longer period of time. These two catalysts were exposed to the synthesis gas with  $H_2:CO=2:3$  molar feed ratio at  $250^\circ C$  and  $260^\circ C$  between about 150 and 400 hours on stream, and then the base conditions ( $250^\circ C$ ,  $H_2:CO=1:1$ ) were repeated. Results at the base conditions at 428-456 h on stream are also shown in Figure V.2-1b and in Table V.2-1. The catalyst with lower potassium content (100 Fe/ 3 Cu/0.2 K) had exhibited remarkable stability and its activity at 430 h on stream was nearly the same as its maximum activity at about 143 h on stream (76.8 vs. 78.1 % ( $H_2+CO$ ) conversion). The catalyst with higher potassium content (100 Fe/3 Cu/0.5 K) had lost nearly 9 % in activity between 143 and 457 h on stream. Although this represents a rather small loss in activity, particularly in view of the fact that the catalyst was exposed to a variety of process conditions during this period of time, the observed trend is nevertheless consistent with literature findings concerning the effect of potassium on catalyst stability. As stated earlier the addition of potassium fosters carbon deposition, and the latter leads to catalyst deactivation by blocking the active sites on the surface (e.g., Kölbel et al., 1951; Anderson et al., 1952; Dry, 1981; Bonzel and Krebs, 1981; Arakawa and Bell, 1983).

The FT reaction on iron catalysts is accompanied by a reversible water-gas-shift (WGS) reaction. One measure of the WGS activity is the  $CO_2$  selectivity defined as the rate of  $CO_2$  production divided by the total rate of CO consumption (or % CO converted to  $CO_2$ ). This assumes that all of  $CO_2$  is produced by the WGS reaction. Another measure of the extent of WGS reaction, expressed as  $P_{CO_2} / (P_{CO_2} + P_{H_2O})$ , is also shown in Table V.2-1. The WGS activity of selected catalysts as a function of reaction temperature is shown in Figure V.2-2. The WGS reaction proceeds nearly to completion ( $CO_2$  selectivity is approximately 0.5) at all reaction temperatures ( $235-265^\circ C$ ) with catalysts which contain potassium as promoter. The WGS activity of the unpromoted iron catalyst increases markedly with the reaction temperature, but even at  $265^\circ C$  the  $CO_2$  selectivity is only 0.41. The WGS activity of the 100 Fe/3 Cu catalyst is significantly greater than that of the unpromoted iron, and approaches the limiting value at  $265^\circ C$ . These results show that both copper and potassium promote the WGS activity of the catalyst, with potassium being the more effective promoter. All catalysts, except the unpromoted iron catalyst attain their steady state WGS activity after about 40 h at  $250^\circ C$  (i.e., 72 hours on stream) as can be seen from Table V.2-1 by comparing  $CO_2$  selectivities at 72 and 142-168 hours on stream.

Our results concerning the promotional effect of potassium on the WGS activity are in





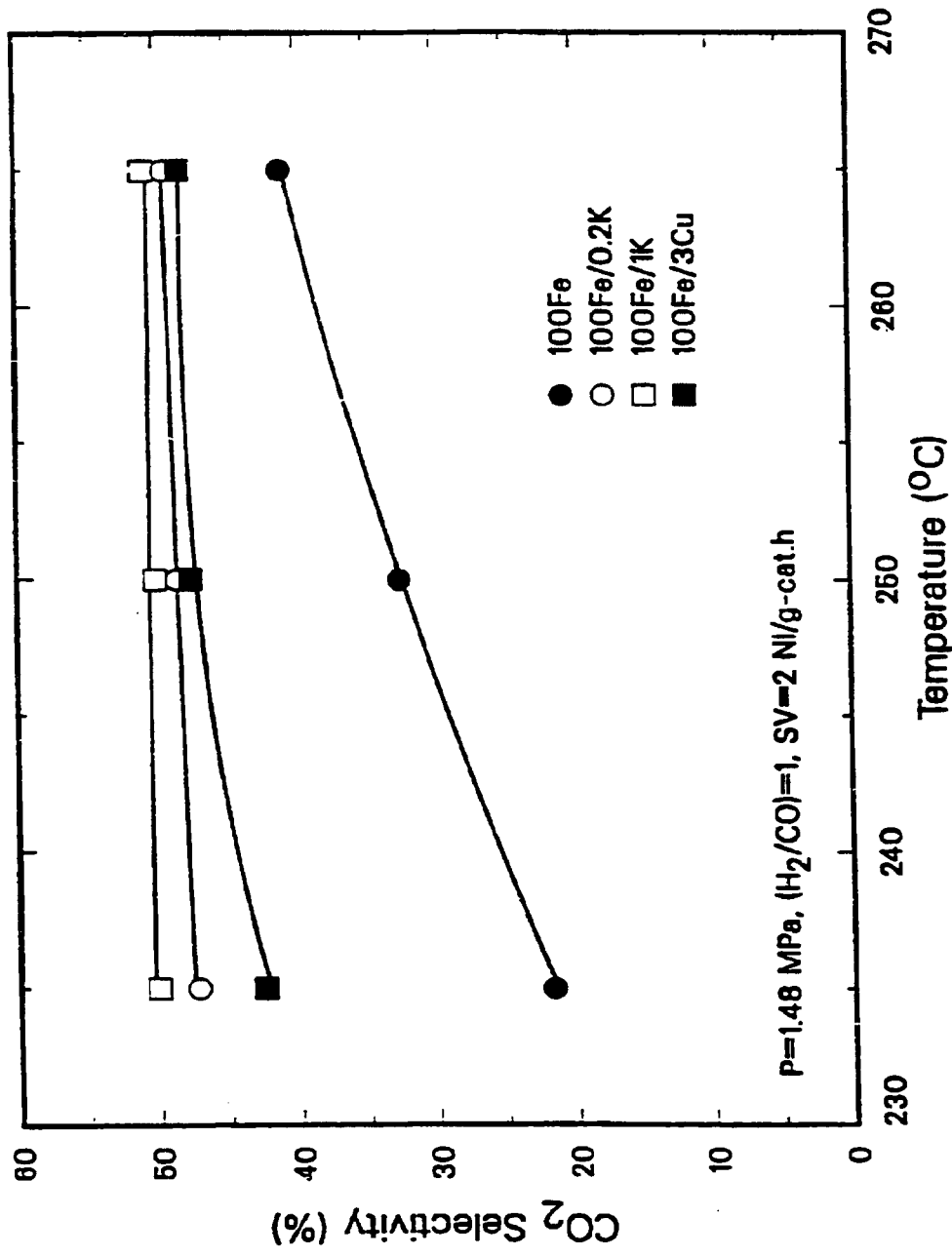


Figure V.2.2. Effect of promoters and temperature on Water-gas-shift activity.

agreement with previous studies (Anderson et al., 1952; Arakawa and Bell, 1983; Dictor and Bell, 1986), but the mechanism by which potassium promotes the WGS activity of iron catalysts is not well understood. We are not aware of any results illustrating the effect of copper on the WGS activity during Fischer-Tropsch synthesis. However, copper is a well known WGS catalyst and the observed effect is as expected.

#### Reproducibility of Results

Before describing results on catalyst selectivity we shall briefly address the important issue of reproducibility of experimental data. In our study, the reproducibility was checked by performing at least two mass balances under the same set of process conditions. As described above, the activity of the catalyst promoted with copper (either singly or doubly) and the unpromoted iron catalyst did not change significantly with time on stream (72 and 143-168 hours). Table V.2-1 shows that product selectivities (hydrocarbon distribution, olefin and oxygenates selectivities) were similar during the two mass balances at the base conditions. With the two doubly promoted catalysts the base conditions were repeated one more time after 430-456 hours on stream, and activities and selectivities were similar to those obtained in the previous two mass balances.

The activity of the three catalysts promoted with potassium alone increased markedly with time on stream (Figure V.2-1b and Table V.2-1). This indicates that these catalysts were undergoing changes in composition with time on stream, leading to increase in the number of active sites. However, there was no significant effect of time on product selectivities for all three Fe/K catalysts, which means that the nature of catalyst sites (or ensembles of sites) did not change significantly with time on stream.

#### Carbon Number Product Distribution

Total product distributions obtained for the various catalysts could not be described by a uniform chain growth probability factor- $\alpha$ . The Anderson-Schulz-Flory plots (mole fraction vs. carbon number) showed two distinct regions of different slopes, and the data were fitted using the three parameter model of Huff and Satterfield (1984) (see Section V.1.3).

Recently, Donnelly et al. (1988) proposed an alternative three parameter model, which is not based on the assumption of existence of the two types of sites. However, the values of  $\alpha_1$  and  $\alpha_2$  obtained from this model and from the previous one are identical. The third parameter in the latter model is the break point between two regions with distinct values of  $\alpha$ . This parameter, designated as  $\xi$  by Donnelly et al., is related to  $\beta$  and if one knows one of them the other one can be calculated.

Representative results, for the three catalysts containing copper, are shown in Figure V.2-3. As can be seen the experimental data are well represented by the above model. The model parameters were estimated using a nonlinear regression subroutine NLIN of the SAS software package. The values of  $\alpha_1$ ,  $\alpha_2$  and  $\beta$  for all catalysts are summarized in Table V.2-2 together with 95% confidence interval limits for these parameters. In the case of the unpromoted iron, the amount of higher molecular weight products collected was too small for accurate determination of model parameters. For products with carbon number greater than 17, the estimated value of  $\alpha_2$  (using the asymptotic method) was greater than 1. The latter value is an indication of problems with product collection and/or analysis. Several authors have reported two chain growth probabilities ("double- $\alpha$ " phenomenon) for unpromoted iron catalysts (Dictor and Bell, 1986; Itoh et al., 1988; Malessa and Baerns, 1988; Donnelly and Satterfield, 1989).

As can be seen from Table V.2-2, no discernible trends can be detected in values of model parameters with the promoter concentrations. In particular, specification of the two chain growth probability values alone (as has been common in the literature) may lead to erroneous conclusions about the product distribution. For example, the values of  $\alpha_1$  and  $\alpha_2$  for the 100 Fe/3 Cu catalyst are greater than the corresponding values for the 100 Fe/3 Cu/0.2 K catalyst (Figure V.2-3 and Table V.2-2). From this one may conclude that the former catalyst produces more higher molecular weight products than the latter (the higher value of  $\alpha$  implies higher probability for the chain growth). However, this conclusion would not be correct as can be seen from Table V.2-1 and Figure V.2-4 where hydrocarbon product distributions for these two catalysts are given. These results can be explained by examining values of the third parameter,  $\beta$ , for these two catalysts. The fraction of sites of type 1 (i.e., sites where the lower molecular weight hydrocarbons are produced) is 0.76 for the doubly promoted catalyst, and 0.99 for the 100 Fe/3 Cu catalyst. This means that with the 100 Fe/3 Cu catalyst the majority of products are produced on the type 1 site, and therefore this catalyst produces more low molecular weight products than the 100 Fe/3 Cu/0.2 K catalyst, even though both  $\alpha_1$  and  $\alpha_2$  are higher for the former than for the latter. Thus, in order to characterize the carbon number product distribution of a given catalyst, it is essential to report values of all three parameters ( $\alpha_1$ ,  $\alpha_2$  and  $\beta$ ). Comparisons of product distributions on different catalysts cannot be made on the basis of values of  $\alpha_1$  and  $\alpha_2$  alone.

#### Hydrocarbon Product Distribution

Figures V.2-4 and V.2-5 show that the average molecular weight of hydrocarbon products

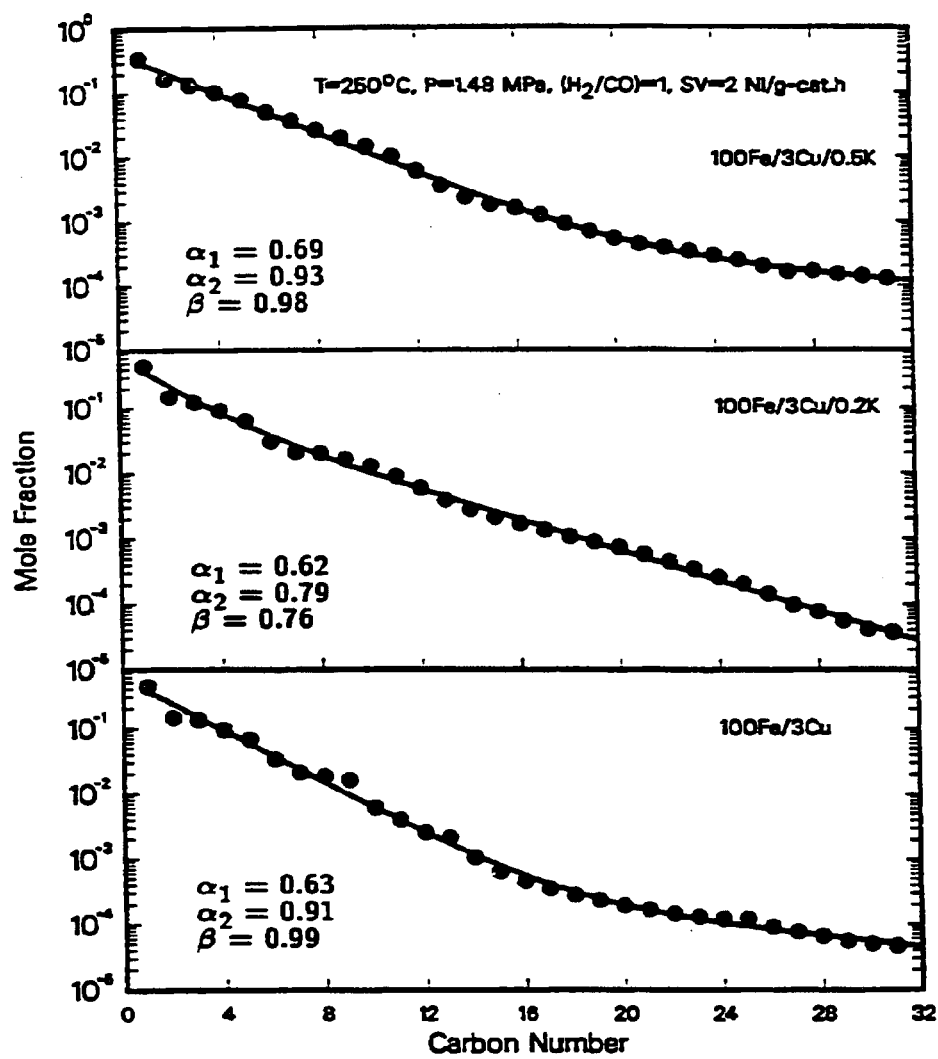


Figure V.2.3 . Anderson-Schulz-Flory distributions for catalysts promoted with copper and potassium.

Table V.2.2. Chain Growth Probability Factors for Different Catalysts<sup>a</sup>

Catalyst	$\alpha_1$ (95% CI) <sup>b</sup>	$\alpha_2$ (95% CI) <sup>b</sup>	$\beta$ (95% CI) <sup>b</sup>
100 Fe	0.50 <sup>c</sup> (0.45-0.67)	<i>d</i>	<i>d</i>
100 Fe/0.2 K	0.61 (0.52-0.69)	0.84 (0.81-0.86)	0.88 (0.78-0.99)
100 Fe/0.5 K	0.68 (0.65-0.70)	0.94 (0.92-0.97)	0.96 (0.95-0.98)
100 Fe/1.0 K	0.66 (0.64-0.68)	0.88 (0.87-0.90)	0.88 (0.84-0.92)
100 Fe/3 Cu	0.63 (0.62-0.65)	0.91 (0.88-0.94)	0.90 (0.89-1.00)
100 Fe/3 Cu/0.2 K	0.62 (0.53-0.70)	0.79 (0.78-0.80)	0.76 (0.66-0.80)
100 Fe/3 Cu/0.5 K	0.69 (0.68-0.71)	0.93 (0.87-0.99)	0.98 (0.97-1.00)

<sup>a</sup> Parameters estimated from products with carbon numbers in the range C<sub>3</sub>-C<sub>30</sub>

<sup>b</sup> 95% Confidence interval

<sup>c</sup> Asymptotic  $\alpha$  value, based on the slope of the product distribution

<sup>d</sup> The three-parameter model could not be used with this catalyst

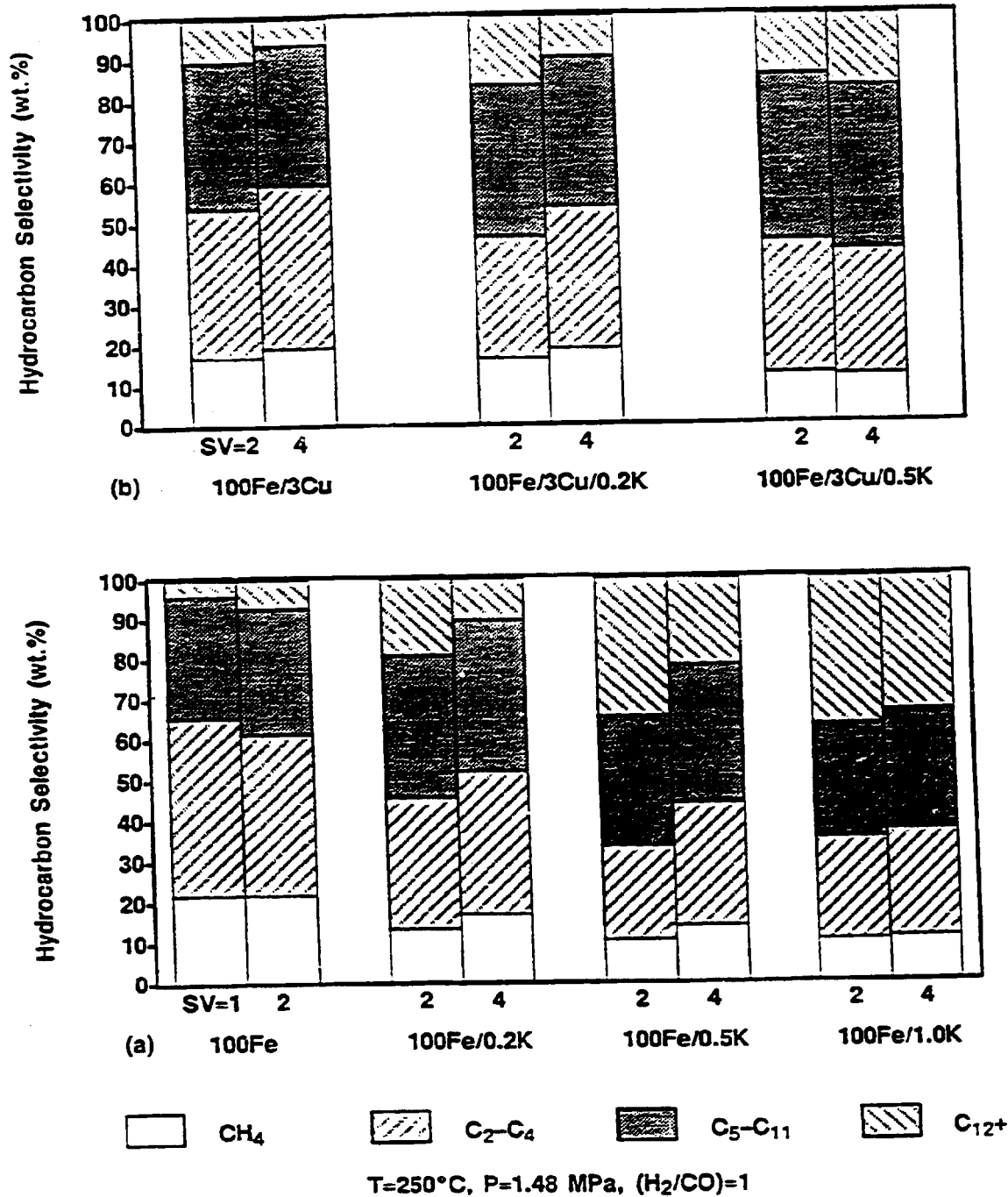
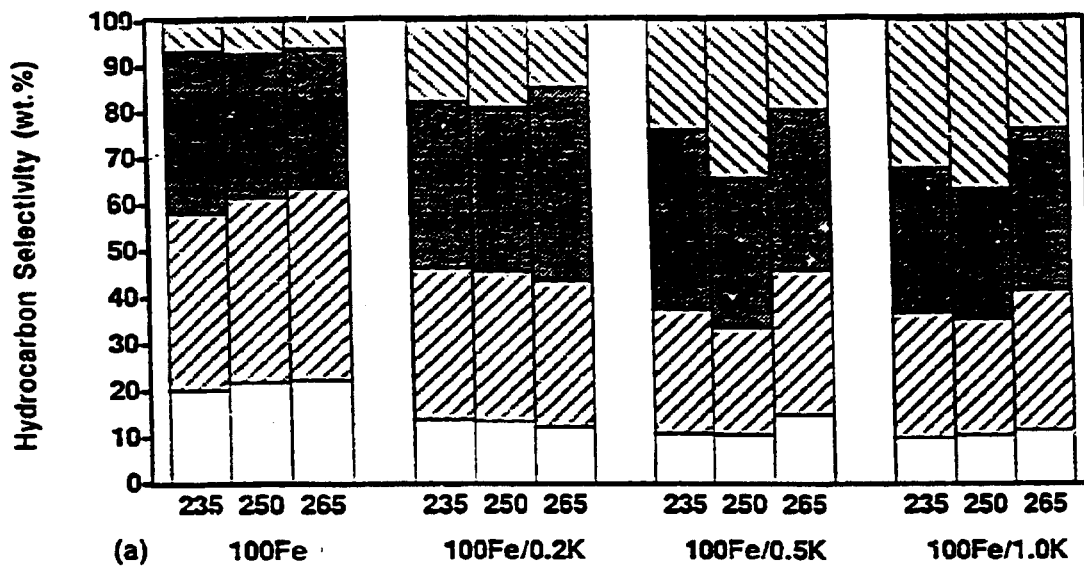
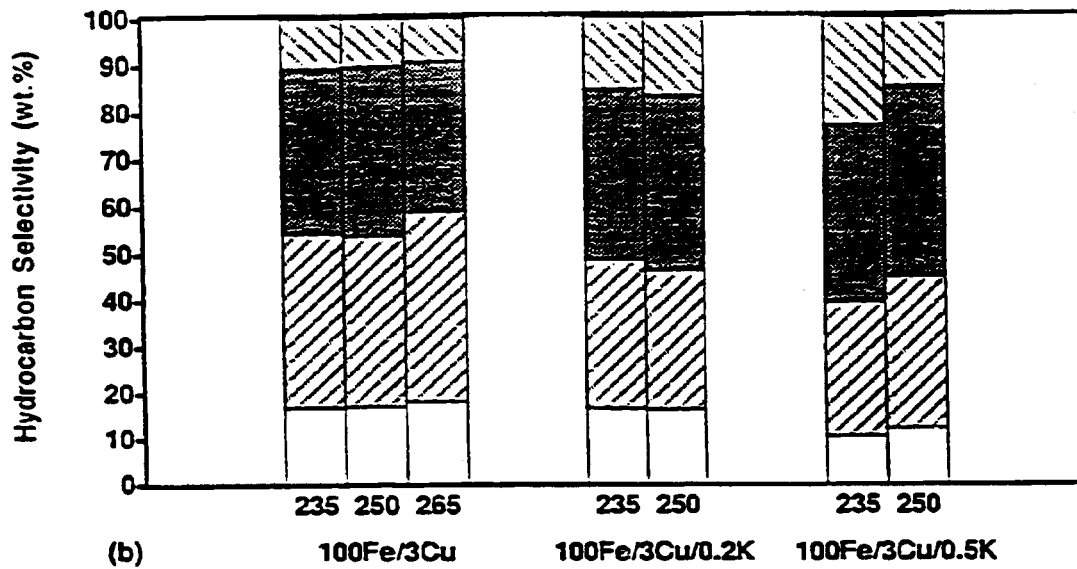


Figure V.24 Effect of potassium content and gas space velocity on hydrocarbon selectivity for (a) singly promoted Fe/K catalysts, and (b) doubly promoted Fe/Cu/K catalysts.



CH<sub>4</sub>
 C<sub>2</sub>-C<sub>4</sub>
 C<sub>5</sub>-C<sub>11</sub>
 C<sub>12</sub>+

P=1.48 MPa, (H<sub>2</sub>/CO)=1, SV=2 NI/g-cat.h

Figure V.2-5 Effect of potassium content and reaction temperature on hydrocarbon selectivity for (a) singly promoted Fe/K catalysts, and (b) doubly promoted Fe/Cu/K catalysts.

increases with addition of either copper or potassium to the unpromoted catalyst. Potassium is a more effective promoter than copper in reducing methane and gaseous hydrocarbon production, while shifting selectivity toward higher molecular weight hydrocarbons (in particular the C<sub>12</sub> fraction). The effect of potassium on hydrocarbon selectivity observed in the present study is in agreement with results obtained in several earlier studies with a variety of iron catalysts (Anderson et al., 1952; Pichler, 1952; Dry, 1981; Arakawa and Bell, 1983; Dictor and Bell, 1986). The increase in average molecular weight of hydrocarbon products is due to increased CO and lower H<sub>2</sub> surface coverage in the presence of potassium. Since chain termination results from the hydrogenation of the iron-carbon bond, the presence of potassium enhances the probability of continued chain growth, i.e., formation of higher molecular weight products (Kölbel and Giehring, 1963; Dry et al., 1969).

The effect of copper on hydrocarbon product distribution during FTS was not studied extensively. Murata (1942), as reported by Anderson (1956, p. 132), made an early study of multipromoted iron-based catalysts and found that the yield of C<sub>5</sub> hydrocarbon products increased with increasing copper content up to about 10 wt%, above which no further selectivity changes occurred. Recently Wachs et al. (1984) reported results from experiments in a fixed bed reactor at 265°C, 7 atm and H<sub>2</sub>/CO=3 at high space velocities (differential CO conversions) with unpromoted Fe and 100 Fe/1.4 Cu catalysts. They found no effect of copper on the product distribution. Additional studies with Fe/Cu catalysts are required in order to elucidate the role of copper in Fischer-Tropsch synthesis.

In our study, it was found that both copper and potassium enhance the selectivity of higher molecular weight products, however the anticipated synergistic effect was not observed in experiments with the two doubly promoted catalysts. Instead, hydrocarbon selectivity of these two catalysts was largely determined by their potassium content, as shown in Figures V.2-4 and V.2-5. Kölbel and Giehring (1963) studied the effect of potassium promotion on activity and selectivity of a precipitated Fe/Cu catalyst containing approximately 0.2 wt% of copper (100 Fe/0.2 Cu/(0 - 0.6) K). They observed also an increase in the formation of higher molecular weight hydrocarbons with increasing potassium content of the catalyst. This general trend was somewhat altered with time on stream, due to more rapid deactivation of catalysts with higher alkali content. They reported that catalysts tend to make more CH<sub>4</sub> and other gaseous hydrocarbons as their activity decreased. A similar trend with time on stream was observed in our study with the 100 Fe/3 Cu/0.5 K catalyst (see Table V.2-1).



The effects of gas space velocity and reaction temperature on hydrocarbon product distribution are illustrated in Figures V.2-4 and V.2-5, respectively. Changes in process conditions had a rather small effect on hydrocarbon product distribution. With the increase in gas space velocity a slight shift toward higher molecular weight products was observed with the unpromoted iron and the 100 Fe/3 Cu/0.5 K catalysts, whereas the opposite trend was observed with all other catalysts. The increase in reaction temperature causes the shift toward lower molecular weight products.

#### Olefin Content (Hydrogenation Activity)

The effect of promoters on olefin selectivity, expressed as a mass fraction of linear olefins in total hydrocarbon product of the same carbon number, is shown in Figures V.2-6a and V.2-6b. All curves are bell shaped, i.e., the olefin content increases from C<sub>2</sub> to C<sub>3</sub>/C<sub>4</sub>, reaches a maximum value, and then decreases with increasing carbon number. This shape results from secondary hydrogenation of olefins. Ethylene is more reactive than other low molecular weight olefins, whereas the increase in hydrogenation activity (i.e., lower olefin content) of higher molecular weight olefins may be attributed to their increased reactivity or to greater adsorptivity of long chain molecules.

Potassium promotion suppresses secondary hydrogenation of olefins and the olefin content increases with the potassium loading as shown in Figures V.2-6a and V.2-6b. This is particularly evident for products which are more susceptible to hydrogenation (C<sub>2</sub> and C<sub>6</sub>). The catalyst containing about 1 wt% of K has the highest olefin content, and the latter does not vary markedly with carbon number. With doubly promoted catalysts potassium promotion becomes effective only at higher loadings. The 100 Fe/3 Cu/0.5 K catalyst has similar olefin content as the 100 Fe/0.5 K catalyst, while the olefin content obtained with the 100 Fe/3 Cu/0.2 K catalyst is nearly the same as that of the unpromoted iron catalyst (Figure V.2-6b). The addition of copper to the unpromoted iron results in increased hydrogenation activity (Figure V.2-6b).

Similar results, concerning the promotional effect of potassium on olefin content and/or its dependence on carbon number, have been reported earlier in the literature (Anderson et al., 1952; Kölbl and Giehring, 1963. Shulz et al., 1982; Dictor and Bell, 1986; Donnelly and Satterfield; 1989). The influence of potassium on secondary hydrogenation of olefins is consistent with its effect on the strength of H<sub>2</sub> and CO chemisorption. In the presence of potassium the CO chemisorption is increased whereas that of H<sub>2</sub> is weakened. This results in

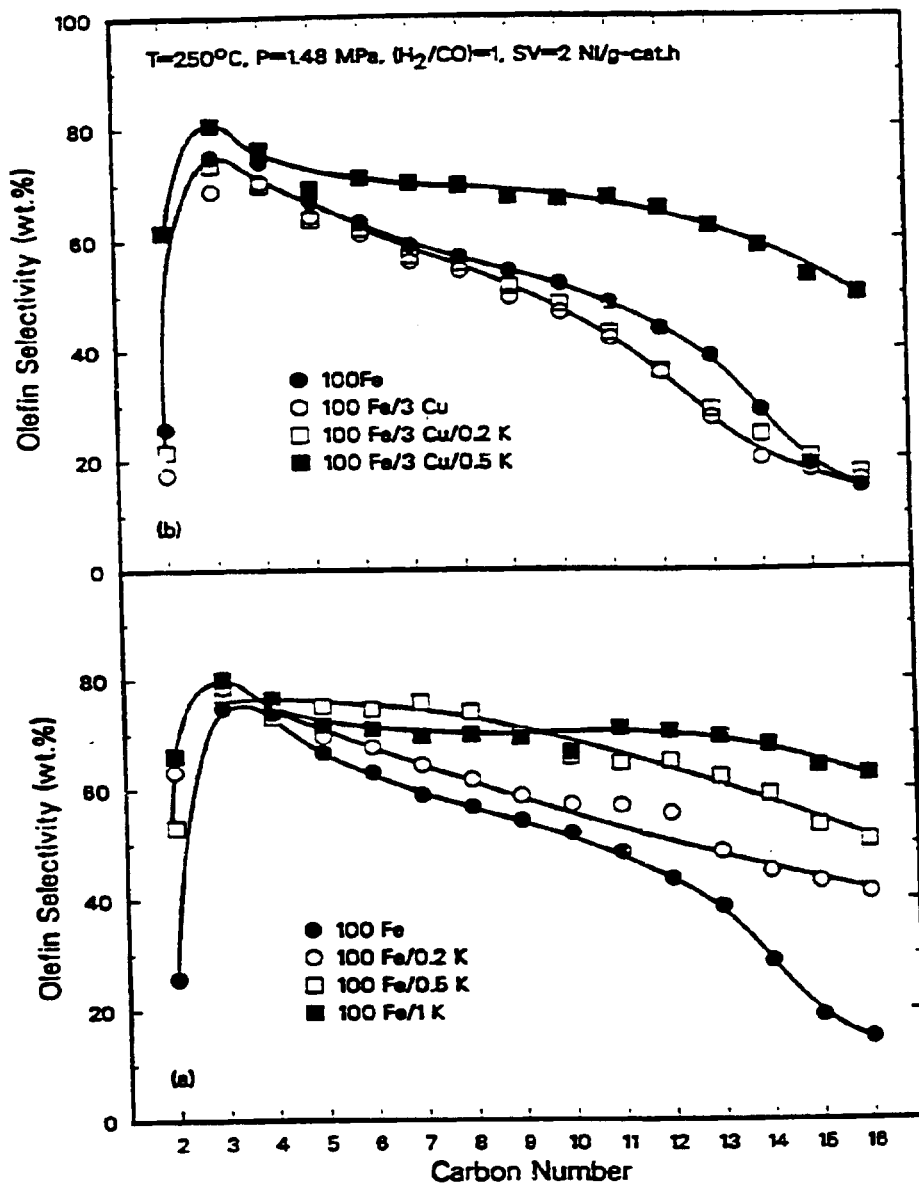


Figure V.2-6. Effect of potassium content on olefin selectivity for (a) singly promoted Fe/K catalysts, (b) doubly promoted Fe/Cu/K catalysts, and comparison with results for unpromoted iron.

lower surface concentration of  $H_2$  and consequently in lower hydrogenation activity (i.e., higher olefin content) of potassium promoted catalysts.

#### Effect of Process Conditions on Olefin Selectivity

The effects of reaction temperature and gas space velocity (gas flow rate) on olefin selectivity of two catalysts (100 Fe/1 K and 100 Fe/3 Cu/0.2 K) are illustrated in Figures (V.2-7a-V.2-7d). The other catalysts followed the same trends observed with either 100 Fe/1 K or 100 Fe/3 Cu/0.2 K but the effects of process conditions were less pronounced. Results obtained with the 100 Fe/1 K catalyst illustrate the behavior of catalysts having low hydrogenation activity (100 Fe/0.5 K, 100 Fe/3 Cu/0.5 K) whereas results from tests with the 100 Fe/3 Cu/0.2 K catalyst illustrate the behavior of catalysts with higher hydrogenation activity (unpromoted iron and 100 Fe/3 Cu).

The olefin content of the 100 Fe/1 K catalyst increased with temperature, whereas the gas flow rate did not have marked effect on olefin selectivity. In studies with the 100 Fe/3 Cu/0.2 K catalyst the olefin content decreased slightly with increase in temperature, and increased ( $C_2$ ,  $C_7$  -  $C_{14}$ ) with increase in space velocity.

The trends shown in Figure V.2-7 can be explained by considering possible effects of reaction temperature and space velocity on primary and secondary reactions. With increasing temperature rates of both primary and secondary reactions are expected to increase, and as a result the olefin selectivity may either increase, decrease or remain constant depending on relative rates of 1-olefin formation (primary reaction) and olefin hydrogenation (secondary reaction). Therefore, the olefin selectivity will increase with increasing temperature on catalysts with high potassium content (low hydrogenation activity), whereas it will remain constant or decrease on catalysts without potassium or those with low potassium content (high hydrogenation activity).

On the other hand, the increase in space velocity will favor primary reactions. Thus, one may expect either an increase (catalysts with relatively high hydrogenation activity) or no change (catalysts with low hydrogenation activity) in olefin selectivity with increasing space velocity.

Results from earlier studies with iron catalysts are generally in agreement with those obtained in the present study and with the preceding discussion. For example, an increase in olefin selectivity with increasing temperature was reported by Dictor and Bell (1986) and Donnelly and Satterfield (1989) on Fe/K catalysts, whereas no effect (Donnelly and Satterfield) or the opposite trend (Dictor and Bell) was found with unpromoted iron catalysts. Schulz et al.

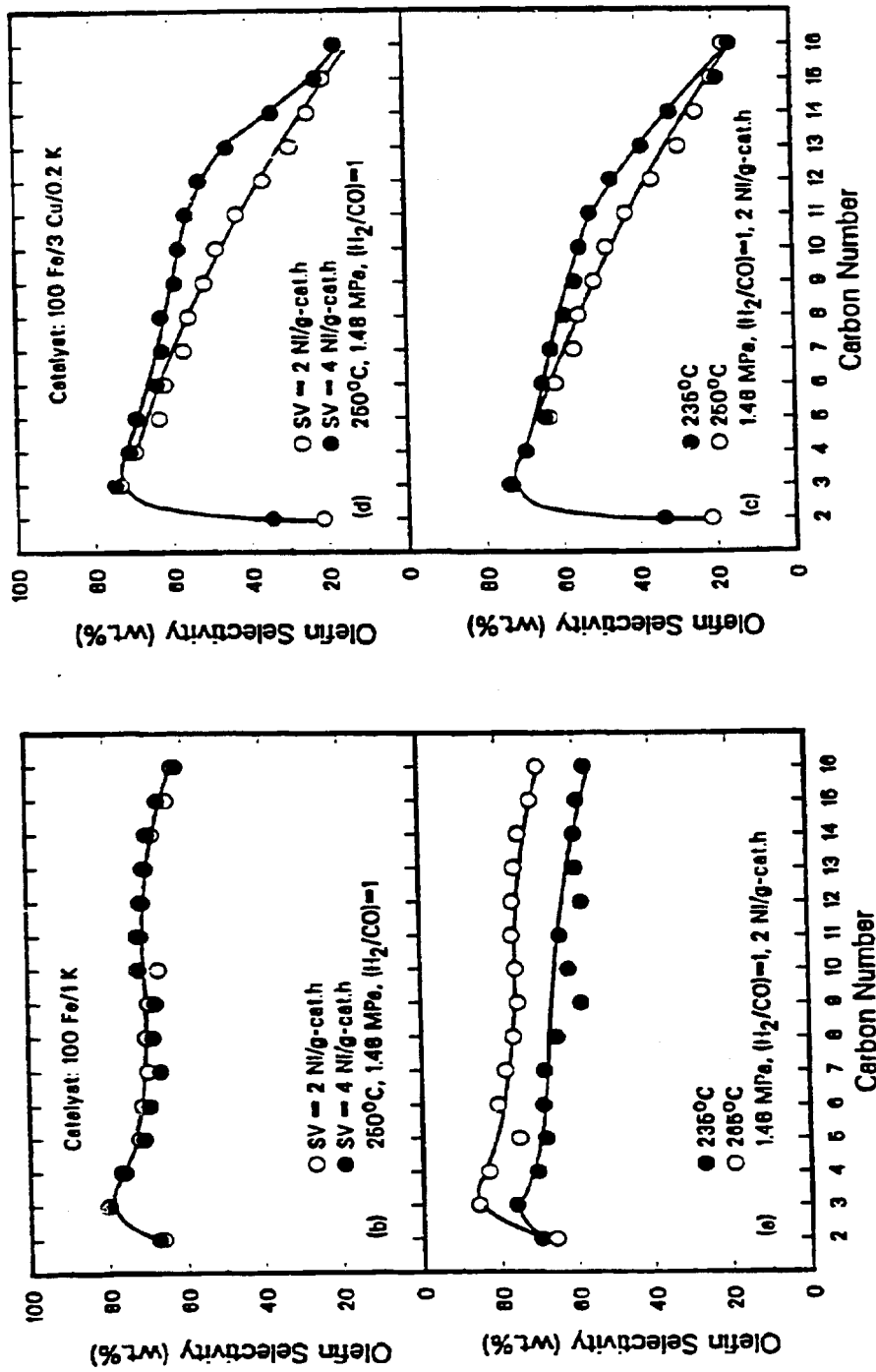


Figure V 2.7. Effect of process conditions on olefin selectivity  
 Influence of temperature, (a) 100 Fe/1 K catalyst, (c) 100 Fe/3 Cu/0.2 K catalyst,  
 Influence of gas space velocity, (b) 100 Fe/1 K catalyst, (d) 100 Fe/3 Cu/0.2 K catalyst.

(1982) reported decrease in olefin selectivity with increasing temperature on an alkali iron catalyst (100 Fe/50 Aerosil/10 Al<sub>2</sub>O<sub>3</sub>/0.3 K). In the latter case the effectiveness of potassium promotion was considerably reduced by presence of silica and alumina as structural promoters.

Increase in olefin selectivity with increasing space velocity was reported in studies by Arakawa and Bell (1983) for both alkali promoted and unpromoted catalysts, and Dictor and Bell (1986) on an unpromoted catalyst, whereas no effect was observed in the latter study with the 100 Fe/0.8 K catalyst, and in the study by Donnelly and Satterfield (1989) with the Ruhrchemie, unpromoted and 100 Fe/1 K catalysts.

#### Olefin Isomerization

Figure V.2-8 illustrates the effect of promoters on olefin isomerization as a function of carbon number. As can be seen, potassium promotion suppresses isomerization of 1-alkenes and for a given catalyst the fraction of 2-alkenes (i.e., isomerization activity) increases with carbon number. For catalysts with higher potassium content (ca. 0.5 - 1 wt% of K) the 2-olefins comprise 2 - 5% of total linear olefins, which suggest that some of the 2-olefins are also formed by primary reactions. The addition of copper enhances the isomerization activity of the unpromoted catalyst (Figure V.2-8b), and has similar effect at low levels of potassium promotion (compare results for 100 Fe/0.2 K and 100 Fe/3 Cu/0.2 K catalysts). However, as the potassium content increases, the effect of copper diminishes, and the fraction of 2-olefins is nearly identical for the two catalysts containing ca. 0.5 wt% of K.

The observed effects of promoters on the extent of isomerization reaction are consistent with the results presented above for olefin hydrogenation, indicating that these two secondary reactions may occur via a common set of intermediates. The latter possibility was suggested by Dictor and Bell (1986) who also proposed a plausible reaction scheme involving an adsorbed primary 1-olefin in a vicinity of an adsorbed hydrogen atom. Therefore, the same arguments that were used above to explain the effects of potassium and carbon number (i.e., molecular weight of olefin) on olefin selectivity can be used to explain the observed effects on olefin isomerization selectivity.

The influence of reaction conditions (temperature and space velocity) was also investigated, and an illustration of the results is presented in Figure V.2-9. Variations in process conditions had negligible effect on olefin isomerization selectivity of the 100 Fe/1 K catalyst. This catalyst has relatively high potassium concentration which suppresses secondary reactions and thus changes in process conditions have very small effect on selectivity. In runs with the 100 Fe/3

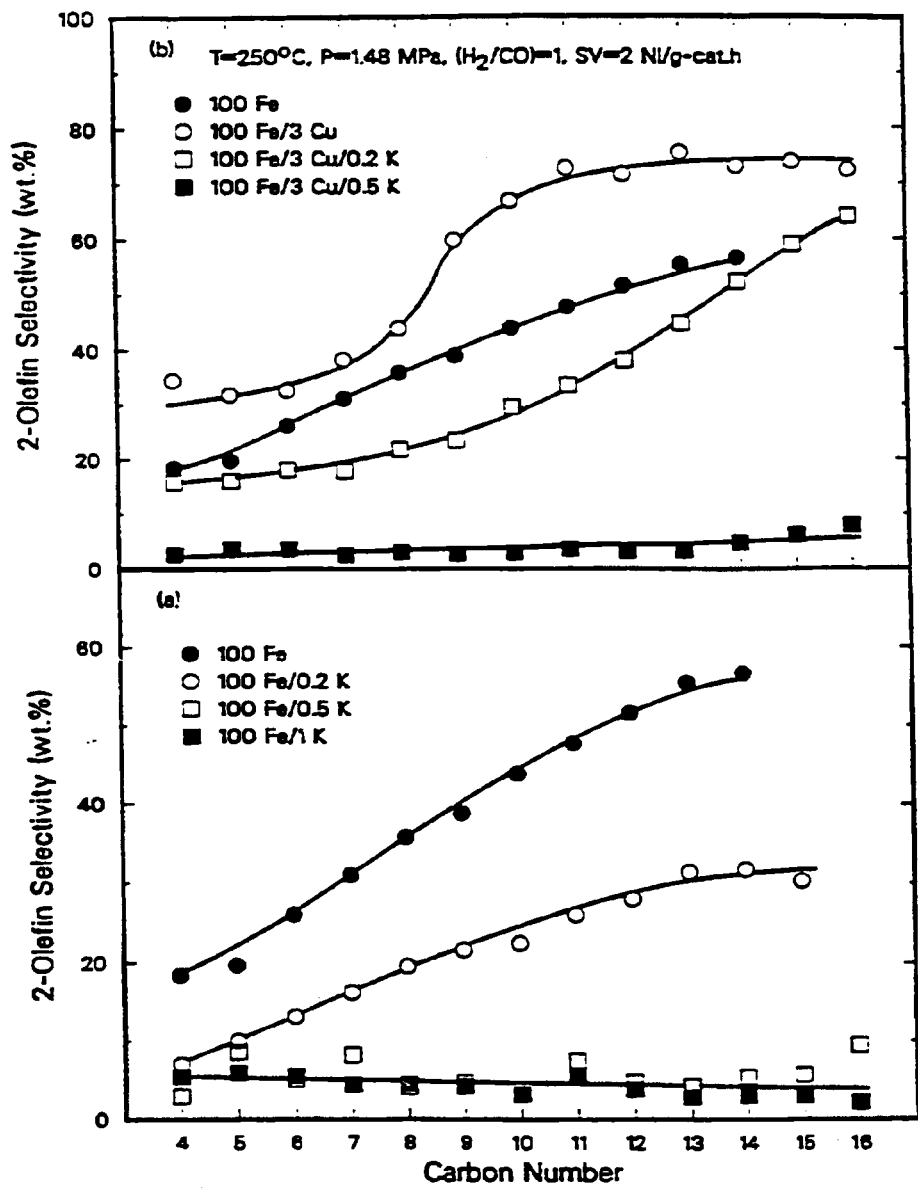


Figure V.2-8. Effect of potassium content on 2-olefin selectivity for (a) singly promoted Fe/K catalysts, (b) doubly promoted Fe/Cu/K catalysts, and comparison with results for unpromoted iron.

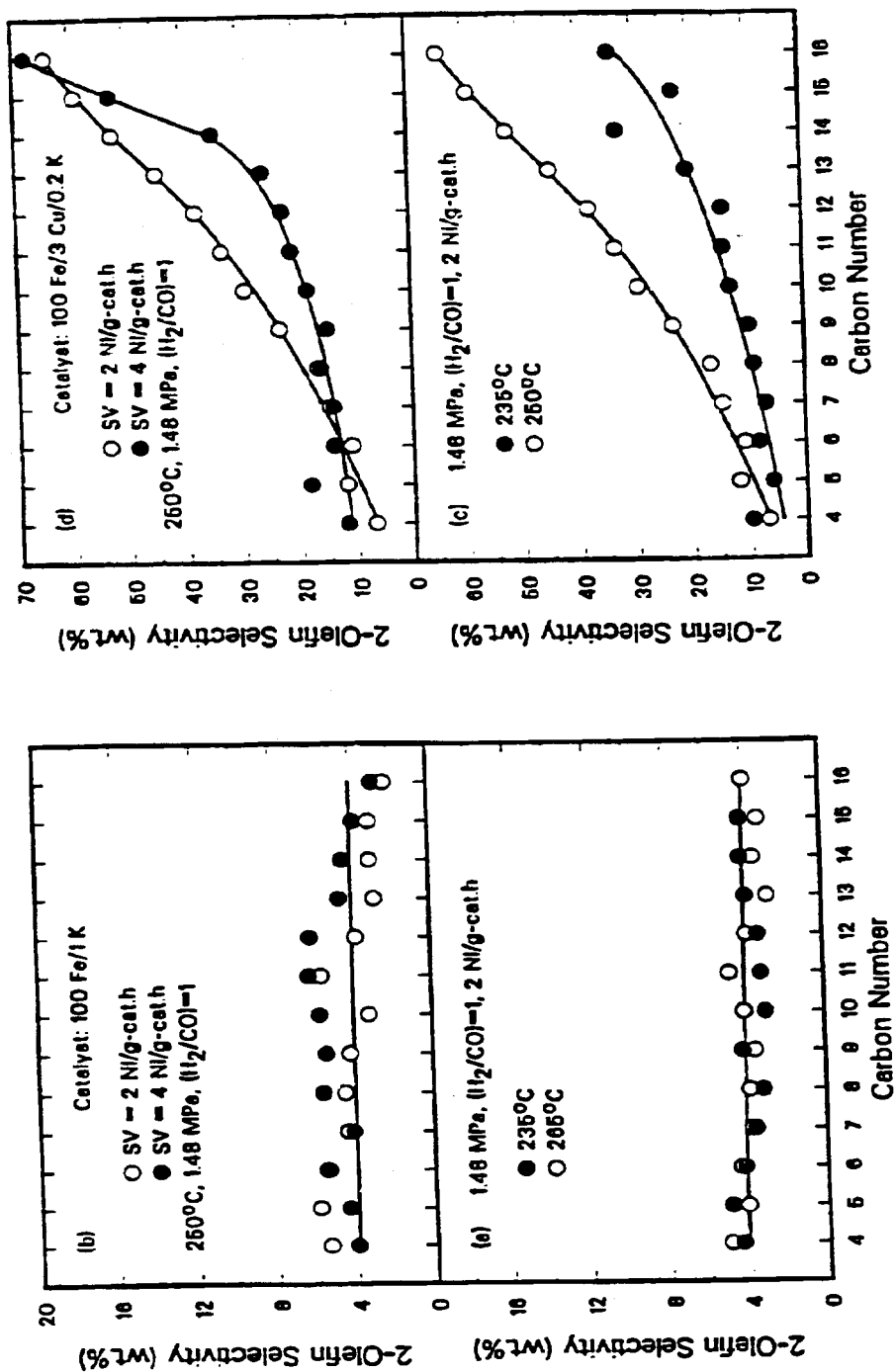


Figure V.2.9. Effect of process conditions on 2-olefin selectivity. Influence of temperature, (a) 100 Fe/1 K catalyst, (c) 100 Fe/3 Cu/0.2 K catalyst. Influence of gas space velocity, (b) 100 Fe/1 K catalyst, (d) 100 Fe/3 Cu/0.2 K catalyst.

Cu/0.2 K catalyst increase in temperature increased the olefin isomerization, whereas increase in space velocity resulted in decrease of olefin isomerization. Both of these observations may be explained in terms of preceding discussion on effects of temperature and space velocity on secondary reactions. Results with other catalysts follow trends observed with either 100 Fe/1 K or 100 Fe/3 Cu/0.2 K catalyst, depending on potassium content of the catalyst.

General trends observed in the present study, on the effects of potassium promotion and reaction conditions on the internal olefin selectivity, are in agreement with those reported in the earlier studies by Schulz and Gokcebay (1984), Dictor and Bell (1986) and Donnelly and Satterfield (1989). In the last study the focus was placed on C<sub>4</sub> olefins only, whereas results illustrating the selectivity of internal olefins as a function of carbon number were presented in the first two studies.

#### Oxygenates Selectivity

The selectivity of oxygenates, expressed as percent of CO converted to oxygenates, is shown in Figure V.2-10 for several catalysts as a function of reaction temperature. Oxygenates comprise only a small fraction of products formed and consist primarily of normal alcohols, and small amounts of aldehydes. No clearly discernible trends are observed in oxygenates selectivity as a function of promoter concentrations, temperature and space velocity. In general, the highest oxygenates selectivity was obtained with the unpromoted catalyst and the 100 Fe/3 Cu/0.5 K catalyst. At some process conditions (235 and 250°C) the selectivity of oxygenates increased with potassium concentration in the 0.2 to 1 wt % range.

An increase in oxygenates with increasing potassium promotion was reported by Anderson et al. (1952) and Dry (1981). Arakawa and Bell (1983) reported increase in ethanol concentration but no effect on methanol, whereas Dictor and Bell (1986) found that potassium promotion suppresses methanol formation and enhances the rate of formation of aldehydes. Both Donnelly and Satterfield (1989), and Dictor and Bell (1986) reported that methanol is essentially the only oxygenated product produced over unpromoted iron whereas other oxygenates were produced on Fe/K catalysts. In contrast to this, in the present study with unpromoted iron catalyst we found not only methanol but other oxygenates as well. In agreement with these authors we found that potassium promotion suppresses formation of methanol and increases selectivity of higher molecular weight alcohols (Figure V.2-11).

From the above, it appears that there are some conflicting reports regarding the effect of potassium on oxygenates selectivity which are to some extent caused by inaccuracies in



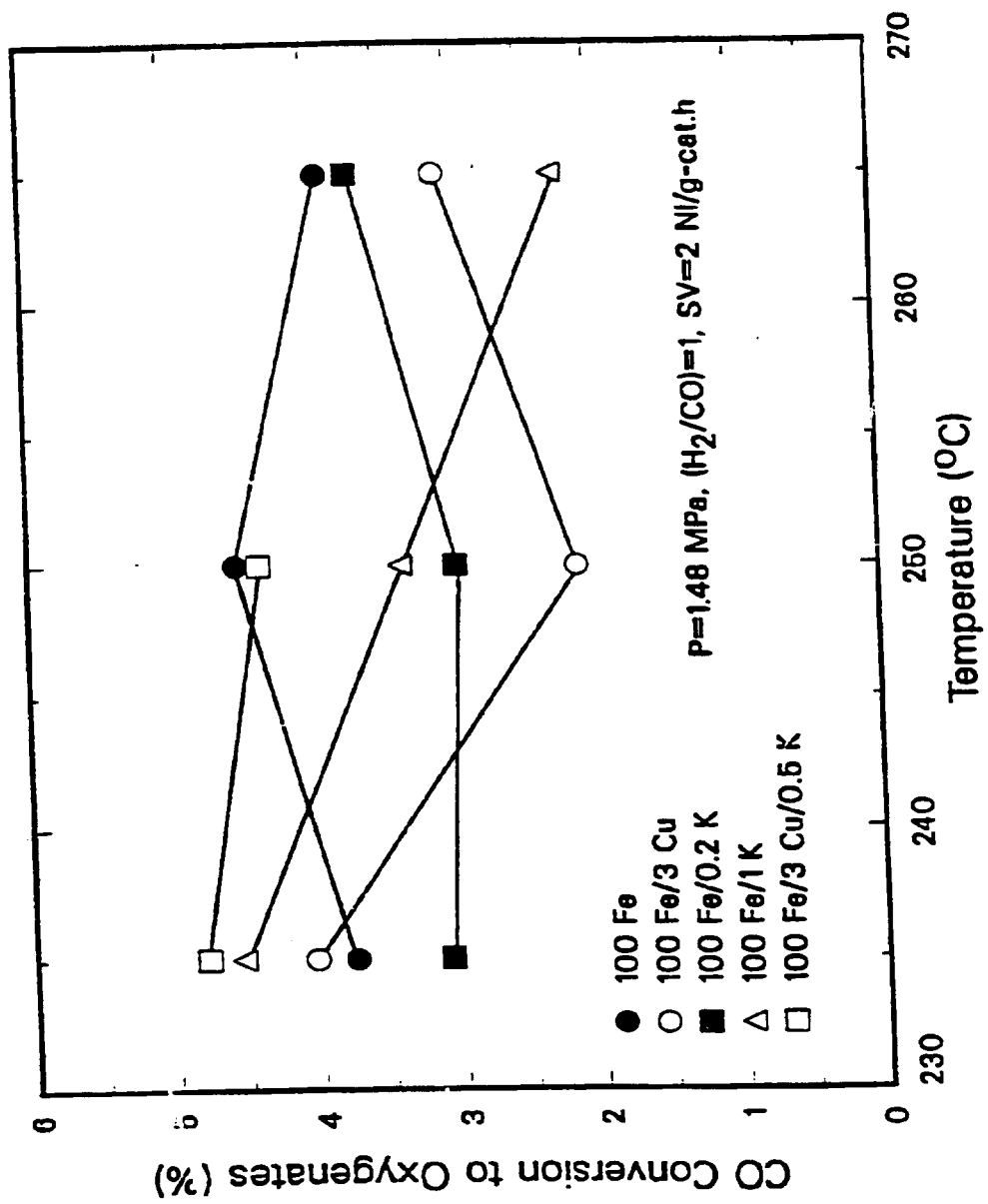


Figure V.2-10 Effect of promoters and temperature on oxygenates selectivity.

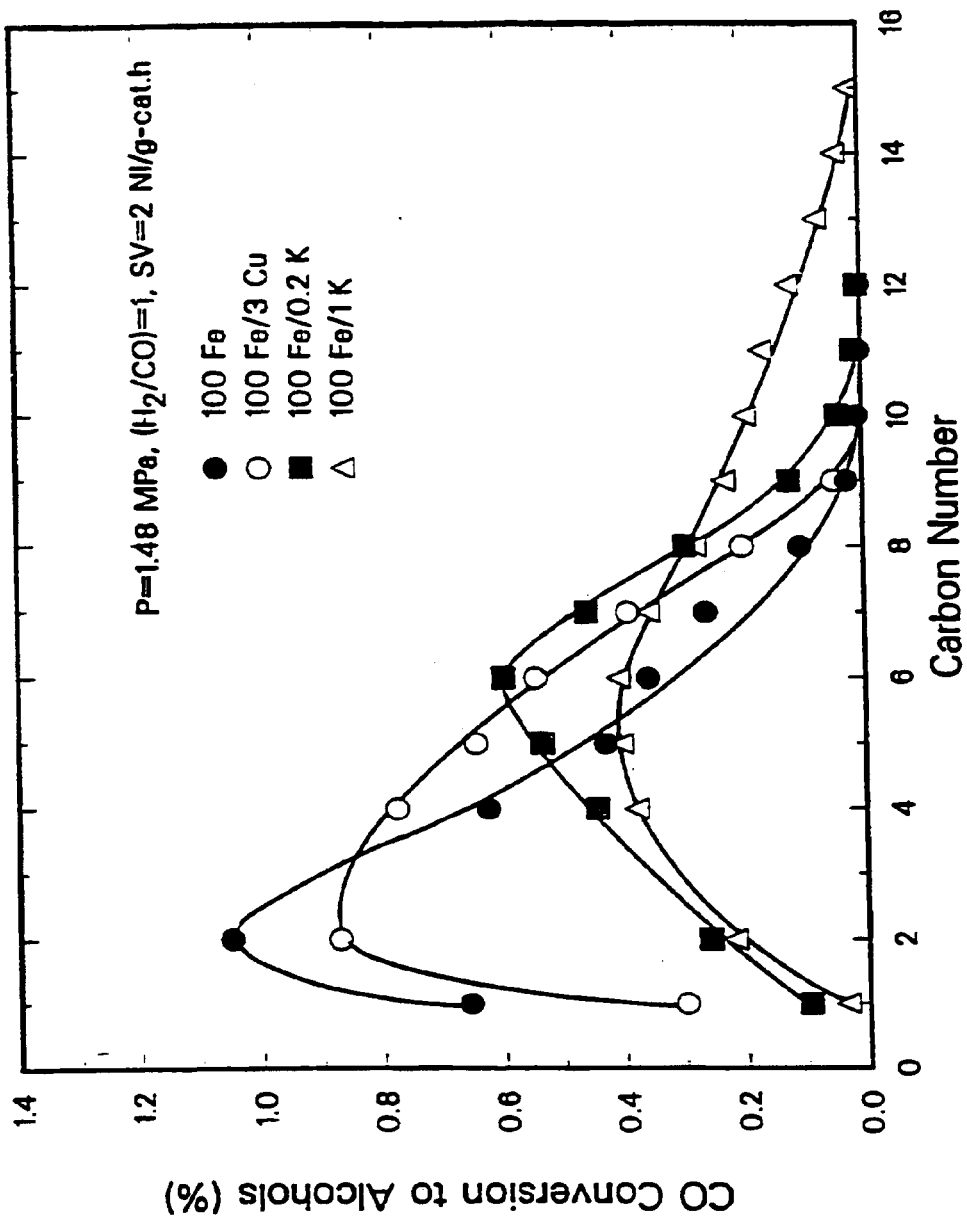


Figure V-2-11. Effect of promoters on alcohol selectivity.