Promoter and Binder/Support Effects
on the Activity and Selectivity of
Precipitated Iron Fischer-Tropsch Catalysts

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ABSTRACT

The effects of potassium and copper promotion, and silica and alumina binders (supports) on activity and selectivity of precipitated iron catalysts for Fischer-Tropsch synthesis (FTS) were studied in a fixed bed reactor It was found that both potassium and copper increase catalyst activity for FTS and the water-gas-shift (WGS) reaction. Potassium promotion (~0.2 - 1 wt%) results in increase in the average molecular weight of hydrocarbon products, and suppression of secondary reactions (olefin hydrogenation, and isomerization of 1 to 2-alkenes). Copper promotion (~3 wt%) has similar effect on hydrocarbon distribution, but it enhances slightly the secondary reactions. The activity of doubly promoted (100 Fe/3 Cu/x K, x=0.2 or 0.5) catalysts was higher than that of singly promoted catalysts and was independent of potassium loading, whereas their selectivity behavior was strongly influenced by their potassium loading.

It was found that both the FTS and the WGS activity decreased with increasing support content. Catalyst deactivation rate decreased with catalysts containing 24 and 100 g of SiO_2 per 100 g of Fe. Secondary reactions increased with increasing silica content. Hydrocarbon selectivities improved (less gaseous hydrocarbons) with the addition of support, except for the catalyst containing 24 SiO_2/100 Fe.

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INTRODUCTION

Slurry phase Fischer-Tropsch processing is considered a potentially economic method to convert coal-derived synthesis gas into liquid fuels. Largely due to its relatively simple reactor design, improved thermal efficiency, and ability to process CO-rich synthesis gas, the slurry process has several potential advantages over conventional vapor phase processes.

While advances have been made in the slurry phase Fischer-Tropsch technology, further work is required to more thoroughly evaluate its potential as a viable technology. Therefore, Air Products and Chemicals, Inc. proposed a program to develop a consistent process/economic data base for a variety of iron-based catalysts. Texas A & M University was the subcontractor for work on development and evaluation of catalysts. This data base allows unambiguous comparison of the performance of the new catalysts tested, both with each other and with the state-of-the-art catalysts compositions. Particular attention was paid to extracting kinetic and selectivity data and developing improved compositions/process parameters. The effects of activation/reduction procedures, promoters and binders/supports on catalyst activity, selectivity and stability were investigated in a systematic way. Results from studies on the effect of activation/reduction procedures were reported at the previous two Contractors' Review Meetings (Bukur et al., 1987, 1988) and elsewhere (Bukur et al. 1989). Here we present recent results on promoter and binder (support) effects.

PROMOTER EFFECT RESEARCH

The most common promoters for iron catalysts are copper and potassium. It is generally believed that copper serves only to promote the reduction of iron during activation, thus allowing lower activation temperatures and consequently, giving less sintering, greater surface areas, and increased activity. Potassium, on the other hand, acts as both structural and chemical promoter, and it affects the catalyst activity as well as the selectivity. Higher potassium concentrations give heavier products (increased wax selectivity) and more olefins in the hydrocarbon products.

Although the qualitative effects of potassium promotion on catalyst activity and selectivity have been clearly established, 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. Our 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.

Catalyst Preparation/Reduction Procedure

Catalysts were prepared using a continuous precipitation method, similar to that described by Kölbel and Ralek (1980). Catalyst precursor was precipitated from an aqueous solution containing iron and copper nitrates at the desired Fe/Cu ratio using aqueous ammonia. After a drying step, the potassium promoter was added as aqueous $KHCO_3$ solution via an incipient wetness pore filling technique. The final step was to dry the catalyst at 120°C for 16 h in a vacuum oven. The catalyst composition was verified in each case using atomic absorption spectroscopy. All catalysts were reduced with hydrogen at 220°C, 500 cm^3/min and atmospheric pressure for 8 h.

Seven catalysts were employed in our 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).

Activity and Stability of Catalysts

Effects of reaction temperature and time on stream at 250°C on FTS activity, measured by (H_2+CO) conversion, are shown in Figures 1a and 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.

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 recrystalization during calcination. Reduced catalysts had maximum metal dispersion at potassium loading 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.

The increase in activity with copper addition that was found in the present study, is in agreement with results obtained in Kölbel et al. (1951) study at 230°C, $H_2/CO=2$ and atmospheric pressure. Kölbel et al. observed increase in overall activity already at very low promoter levels (ca. 0.1 wt% of Cu), and further increases in the copper level had no additional effect. 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 extent of metal reduction (Dry, 1981). This suggests that higher activity of Fe/Cu catalysts relative to unpromoted iron may be attributed to differences in the size and number of α-Fe and/or iron carbide crystallites during synthesis. Also, following the reduction with H_2 at 220°C, the copper containing catalysts have a larger fraction of metallic iron than the unpromoted iron and the Fe/K catalysts. This may also be responsible for their higher activities, since the zero-valent iron is more active for the FTS synthesis than the iron in higher oxidation states (Fe(II) or Fe(III)).

The effect of time on stream on FTS activity at 250°C and 2 Nl/g-cat•h is illustrated in Figure 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 unpromoted 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 1b (100 Fe/0.5 K) and Table I (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 at 300°C, conducted in Chemistry Department at Texas A&M University, 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 (Li, 1988). This explains the fact that the induction period during FTS 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°C and 260°C between about 150 and 400 hours on stream, and then the base conditions (250°C, H_2:CO=1:1) were repeated. Results at the base conditions at 428-456 h on stream are also shown in Figure 1b and in Table I. 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. 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; Arakawa and Bell, 1983).

The FTS 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. The WGS activity of selected catalysts as a function of reaction temperature is shown in Figure 2. The WGS reaction proceeds nearly to completion (CO_2 selectivity is approximately 0.5) at all reaction temperature (235-265°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°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°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°C (i.e., 72 hours on stream) as can be seen from Table I by comparing CO_2 selectivities at 72 and 142-168 hours on stream.

Hydrocarbon Product Distribution

Figure 3 shows that the average molecular weight of hydrocarbon products increases with addition of either copper or potassium to the unpromoted catalyst. Potassium is more effective promoter than copper in reducing methane and gaseous hydrocarbon production, while shifting selectivity toward higher molecular weight hydrocarbons (in particular the C_{12}^+ 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; Dry, 1981; Arakawa and Bell, 1983). The increase in average molecular weight of hydrocarbon products is due to increased CO and lower H_2 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.

The effect of copper on hydrocarbon product distribution during FTS was not studied extensively. Murata, as reported by Anderson (1956, p. 132), made an early study of multipromoted iron-based catalysts and found that the yield of C_5+ 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 $H_2/CO=3$ 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 Figure 3. The effect of reaction temperature on hydrocarbon product distribution is also illustrated in Figure 3. 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 4a and 4b. All curves are bell shaped, i.e. the olefin content increases from C_2 to C_3/C_4, 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 4a and 4b. This is particularly evident for products which are more susceptible to hydrogenation (C_2 and C_6^+). 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 4b). The addition of copper to the unpromoted iron results in increased hydrogenation activity (Figure 4b).

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; Shulz et al., 1982; Sudheimer and Gaube, 1985; Dictor and Bell, 1986). The influence of potassium on secondary hydrogenation of olefins is consistent with its effect on the strength of H_2 and CO chemisorption. In the presence of potassium the CO chemisorption is increased whereas that of H_2 is weakened. This results in lower surface concentration of H_2 and consequently in lower hydrogenation activity (i.e. higher olefin content) of potassium promoted catalysts.

Olefin Isomerization

Figure 5 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 5b), 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.

Promoter Effect Research - Conclusions

Promotion of iron with potassium in the range 0.2 – 1 wt%, increases activity of the Fischer-Tropsch and water-gas-shift reactions, and the average molecular weight of hydrocarbon and other organic (primarily alcohols) products. It also causes suppression of olefin hydrogenation and isomerization reactions. Potassium promotion inhibits iron reduction and as a result the potassium promoted catalysts require longer time to achieve the steady state activity.

Promotion of iron with copper (100 Fe/3 Cu) also increases rates of FTS and WGS reactions. Copper is more effective promoter than potassium in increasing the rate of FTS, whereas the opposite applies to the WGS activity. Also, promotion with copper facilitates reduction of iron and thus decreases time required to achieve the steady state activity. In the presence of copper the hydrocarbon product distribution shifts toward higher molecular weight products, but the magnitude of changes is significantly smaller than that observed with potassium promotion. Copper promotion enhances slightly the secondary reactions (olefin hydrogenation and isomerization).

The FTS activity of the two doubly promoted catalysts (100 Fe/3 Cu/0.2 K and 100 Fe/3 Cu/0.5 K) was independent of their potassium content and higher than that of any of the singly promoted catalysts. In tests over a long period of time (up to 460 hours on stream) the catalyst with higher potassium content had lost about 9% of its maximum activity, whereas the 100 Fe/3 Cu/0.2 K catalyst had lost only 2%. The WGS activity of the doubly promoted catalysts was similar to that of the Fe/K catalysts. Selectivity behavior of the doubly promoted catalyst was strongly influenced by their potassium content. The catalyst containing ~0.2 wt% K had selectivities (hydrocarbon product distribution, olefin content) similar to that obtained with the 100 Fe/3 Cu catalyst, whereas the 100 Fe/3 Cu/0.5 K catalyst had selectivities similar to that obtained with the 100 Fe/0 5 K catalyst. This shows that, in the presence of copper, higher potassium loadings are needed to achieve promotional effects on product selectivity. Reaction studies of the type presented in this paper coupled with detailed catalyst characterization studies are needed to gain better understanding of the role of promoters in iron catalysts for the Fischer-Tropsch synthesis.

BINDER/SUPPORT RESEARCH

Supported catalyst systems with high support-to-mental ratios have not been overly effective in yielding good Fischer-Tropsch synthesis performance. In the slurry phase process, supported catalysts reduce the bulk concentration of metal and thus may hinder mass transfer of gas to liquid as solids loadings are increased to maintain metal concentrations. On the other hand, supported systems may actually increase the concentration of active metal sites by maintaining higher metal dispersions. The nature of the support is also important, since acidic sites on the support can render basic promoters like potassium ineffective, preventing interaction between promoter and metal. Previous work at SASOL (Dry, 1981) in fixed bed reactors, examined the effects of promoters and supports on the performance of Ruhrchemie-type precipitated Fe catalysts. In one set of experiments, a series of Fe/Cu/K_2O precipitates was prepared using Cr_2O_3, MgO, Al_2O_3 or ZnO in place of the silica. None of these catalysts was as active as the standard SiO_2-containing material. An supported composition was also less active. Compositions containing both SiO_2 and a second support material also showed lower performance. Of all the supports, small amounts of added Al_2O_3 resulted in the lowest wax selectivity without excessive deactivation. This concept could be used to control selectivity to some extent.

A brief examination of promoted iron catalysts containing silica or alumina as binder/support has been made in our laboratory. Selected results from tests in fixed bed reactors are described and discussed.

Catalyst Preparation/Reduction Procedure

Catalyst preparation involved three steps: preparation of the iron-copper precursor, incorporation of binder/support (silica or alumina), and finally potassium impregnation. After the impregnation the catalyst was dried and calcined in air at 300°C for 5 h, and then crushed and sieved to a diameter between 0.25 and 0.55mm (30/60 mesh). All catalysts were reduced with carbon monoxide at 280°C and atmospheric pressure for 12 hours.

Six catalysts were employed in the present study: an unsupported iron/copper/potassium catalyst (100Fe/5Cu/4·2K in parts per weight), three silica-supported catalysts (100Fe/5Cu/4·2K/xSiO_2, where x=8, 24 and 100), and two alumina-supported catalysts (100Fe/5Cu/4·2K/xAl_2O_3, where x=8 and 24). The technique used to prepare the alumina-containing catalysts could attain a maximum concentration of only about $30Al_2O_3/100Fe$, so a catalyst with high alumina concentration ($100Al_2O_3/100Fe$) was not available for testing.

Catalyst Characterization

The metal concentrations in the catalyst were determined by atomic absorption analysis using a Varian Spectra AA 30 absorption spectrophotometer. The following techniques were used to characterize selected catalysts after calcination and CO reduction:

(i) Surface area measurements utilizing the BET method on a Quantachrome-Quantasorb apparatus;

(ii) Pore Size Distribution by mercury porosimetry on a Micromeritic Pore Sizer 9310;

(iii) Temperature programmed/isothermal reduction;

(iv) Temperature programmed desorption of H_2;

(v) X-ray photoelectron spectroscopy on a Hewlett-Packard (Model 5950A) ESCA spectrometer.

Each catalyst preparation was analyzed for actual iron, copper, potassium, and silica or alumina contents by atomic absorption spectroscopy. Table II summarizes the intended nominal and actual analyzed composition of each catalyst used in this study. For purposes of simplicity, each catalyst will be referred to by its nominal composition. Total surface areas, determined by application of the BET method to N_2 adsorption isotherms at -196°C, were obtained for the unsupported and silica-supported catalysts, following reduction treatment in CO at 300°C. These data, also presented in Table II, demonstrate that increasing content of SiO_2 support results in substantial increase in catalyst surface area. In addition to surface area measurements, mercury porosimetry was employed to obtain the pore size distributions of calcined and reduced catalysts.

Following calcination and subsequent reduction in CO for 4 h at 300°C, the distribution of the pore volume for each of the three silica-supported catalysts differed, depending upon SiO_2 content. The $8SiO_2$ material exhibited a well-defined maximum at a pore diameter of 150-200 Å, while the $24SiO_2$ and $100SiO_2$ catalysts displayed bimodal pore size distributions. In addition to a maximum at ~ 100 Å, each of the latter two materials had a substantial fraction of its total pore volume accounted for by pores $\leq$ 60 Å in diameter (the lower limit of detection of the porosimeter employed for these measurements). The $8Al_2O_3$ catalyst displayed a broad pore size maximum centered at ~ 125 Å, while the $24Al_2O_3$ catalyst showed a maximum at $<$ 60 Å.

The fractional metal exposures shown in Table II were determined by temperature -programmed desorption of H_2 from catalysts that had previously been reduced in CO at 300°C. Reduced samples were heated to 300°C in a flowing 5% H_2/N_2 gas mixture, and then cooled to ambient temperature under the same gas stream to effect saturation of metallic surface sites with dissociatively adsorbed hydrogen. The carrier gas flow was then switched to pure N_2 and the sample temperature increased at 20°C/min. The total amount of thermally desorbed H_2 evolved during this treatment was quantitatively measured and used to calculate the number of exposed metallic iron sites by assuming a stoichiometry of one adsorbed hydrogen atom per site. The low metal exposure (.015) determined for the silica-free catalyst is typical of those observed for unsupported iron. The presence of 8 and 24 parts of SiO_2 support, however, caused only slight increases in metal exposure (to .022 and .021, respectively). Despite the higher surface areas of these materials, which enable more effective dispersion of supported metal crystallites, the extent of iron reduction to the metallic state (required to chemisorb H_2) is substantially lower than that of the unsupported catalyst (*vide infra*), resulting in correspondingly decreased H_2 uptakes. The exposures observed for the catalysts containing 8 and 24 parts of Al_2O_3 support (.040 and .055, respectively) are markedly larger than those of their silica-supported counterparts.

<u>Programmed/Isothermal Reduction Behaviors</u>

CO reduction profiles at 300°C of the calcined, unsupported 100Fe/5Cu/4.2K catalyst and of four of the supported catalysts used in this study are shown in Figure 6. The sharp maximum in reduction rate that occurs at 12 to 15 min of reaction in each of the profiles is due to the first step of the characteristic two-step reduction process of Fe_2O_3 (Br[illegible] et al. 1982; Hughes et al. 1987). The small shoulder that is visible on the left side of these peaks results from reduction of the copper promoter, which subsequently facilitates the onset and increases the rate of iron reduction. According to the nucleation theory, the reduction of oxide accelerates as the first metal nuclei are formed. The lower reduction temperature required for copper oxide relative to iron oxide leads to formation of nucleation sites in metallic copper at temperatures where metallic iron would not normally be formed. This increase in the number of nucleation sites accelerates the subsequent reduction of iron oxide. It should be noted that, except for the catalyst containing 100 parts of SiO_2 support (profile (d)), the first step of iron reduction is relatively unaffected by the identity or amount of support material.

The broad peak having a maximum at ~ 20 min in profile (a) corresponds to subsequent reduction of Fe_3O_4 to metallic iron. Following the maximum, the rate of this second reduction step for the unsupported catalyst slowly decreases and reaches zero after ~ 70 min of treatment. Total amounts of CO consumed (as determined from the calibrated areas of the two reduction peaks) indicate that the two bulk-phase reduction steps for the unsupported catalyst both proceed to ≥ 95% of stoichiometric completion. (By contrast, the second reduction step for a corresponding *unpromoted* iron precipitate, not shown in Figure 6, required > 180 min to complete under the same conditions.)

The inhibiting effect of increasing contents of silica support on the second step of iron reduction is clearly illustrated by profiles (b), (c), and (d) in Figure 6. The reduction behavior of the catalyst containing 8 parts SiO_2 (b) closely resembles that of the unsupported catalyst (a), although the second reduction step results in only ~ 75% reduction to metallic iron. The presence of 24 and 100 parts SiO_2 (profiles (c) and (d), respectively) cause increasing suppression of the second step of bulk iron reduction. The extent of reduction to metallic iron attained only ~ 25% for the $24SiO_2$ catalyst and < 10% for the $100SiO_2$ material. Reduction behavior of the $8Al_2O_3$ catalyst (profile (e)) resembles those of the unsupported and $8SiO_2$ catalysts, with the second step of reduction corresponding to ~ 90% of stoichiometric reduction to metallic iron.

Surface Composition

The programmed/isothermal reduction studies described above reveal overall bulk-phase reduction behaviors of the iron catalysts. In order to obtain additional information about extent of iron reduction and catalyst composition in the near-surface region, where adsorption and catalysis occur, XPS spectra were obtained for selected catalysts employed in this study. Table III summarizes the relative amounts of Fe^0 and Fe^{n+} that were observed following reduction in CO for 12 h at 300°C. The fractional contents shown are based on relative areas of the Fe $2p_{3/2}$ peaks at binding energies of 707 ± 0.5 eV (Fe^0) and 711 ± 0.5 eV (Fe^{3+}/Fe^{2+}). The observed trends in extent of surface iron reduction revealed by XPS measurements correlate well with those determined from bulk-phase reduction studies of the silica-supported catalysts. Extents of reduction to surface metallic iron are, in general, lower than those measured for the bulk phase. XPS results for the alumina-supported catalyst indicate that the extent of reduction to zero-valent surface iron is substantially lower than that in the bulk. In all cases, subsequent exposure of CO-reduced catalysts to a 2/1 mixture of H_2/CO at 250°C and atmospheric pressure caused substantial re-oxidation of reduced iron by the water formed during the FTS reaction. This observation is consistent with the fact that treatment of any of these precipitated iron catalysts in H_2 at 300°C results in much lower extents of reduction to metallic iron than do the corresponding treatments in CO reported here, due to re-oxidation by the water by-product of H_2 reduction (Li, 1988).

The potassium/iron surface ratios contained in Table III are based on integrated areas of the K $2p_{2/3}$ peak at 293 eV and the Fe $2p_{2/3}$ peak described above. The iron and potassium peak areas were not corrected for differing atomic sensitivity factors, due to the multiplex of iron oxidation states. Hence, although the ratios shown do not represent quantitative surface atomic compositions, they do reveal comparative differences among the various catalysts studied. It should be noted that the K/Fe ratios of the $8SiO_2$, $8Al_2O_3$, and $24Al_2O_3$ catalysts (0.2, 0.2, and 0.5, respectively) are substantially larger than those of the $24SiO_2$ and $100SiO_2$ materials, both of whose K $2p_{3/2}$ peaks were too small to obtain accurate integrated areas. The larger ratios observed for the former group of catalysts suggests that the potassium promoter is more highly distributed on the surfaces of these materials than on those of the two high-silica catalysts

Catalyst Activity and Stability

The effects of gas space velocity and support type and content on catalyst activity, expressed in terms of (H_2+CO) conversion, are shown in Figure 7. The specific FTS activity decreased with increase in space velocity, and with addition of the support. The unsupported catalyst and the two catalysts containing 8 parts of support (SiO_2 or Al_2O_3) had similar activities. While the BET surface areas of the reduced SiO_2-containing catalysts increased with support content (Table II), the (H_2+CO) conversions decreased at all conditions tested. The increased BET surface areas are caused by addition of high surface area binder but, as discussed above, the latter did not result in a marked increase of the active metal surface area. Based on the catalyst characterization results above, the lower activities of catalysts containing 24 or more parts of support per 100 parts of iron may be attributed to increased intraparticle diffusional resistance (smaller pore diameters) and incomplete reduction.

In contrast to our results, Egiebor and Cooper (1985) found that the reactant conversions changed only slightly as the support concentration increased from 21 to 73 parts of SiO_2 per 100 parts of Fe. The (H_2+CO) conversions in tests conducted at 0.7 MPa, 300°C, 240 h^{-1} and $H_2/CO = 1$, were between 51.4 and 54.5%. These conversions are similar to that obtained in our study with the $24SiO_2/100Fe$ catalyst at 235°C, indicating that our catalyst was more active. The differences in trends (activity vs. support concentration) in Egiebor and Cooper's study and in the present one are caused by significant differences in methods of catalyst preparation and activation procedures employed.

The baseline conditions in our study were repeated between 143 and 169 h on stream, and the activity of all catalysts had declined (Table IV). The unsupported catalyst, the $8SiO_2/100Fe$ catalyst and the two alumina-containing catalysts had lost between 40 and 54% of their activity after 40-48 h on stream, whereas the loss in activity was much smaller (~12%) with catalysts containing 24 and 100 parts of SiO_2 per 100 parts of Fe. The $24SiO_2/100Fe$ catalyst exhibited excellent stability during tests in fixed bed and slurry bed reactors at 250°C, 1.5 MPa, 2 nL/g-cat/h and $H_2/CO = 0.67$ over a period of 480 h, as reported elsewhere (Bukur et al., 1988). Results from the fixed bed reactor tests are shown in Figure 8. The loss in activity may be attributed in part to the high potassium content of these catalysts, since potassium fosters carbon deposition which, in turn, blocks the active sites on the surface. The increase in stability with addition of silica support may be the result of stabilization of iron crystallites during synthesis and/or interaction between the potassium and silica. The latter decreases the surface basicity of the catalyst and thus reduces the rate of carbon deposition.

Water-Gas-Shift Activity

The effects of reaction temperature and support type and content on the water-gas shift (WGS) activity are shown in Figure 9, where the CO conversion to CO_2 (CO_2 selectivity) is used as a measure of the WGS activity. The WGS activity increased with temperature for all catalysts, and decreased with increasing silica content. The unsupported catalyst, the two alumina-supported catalysts and the $8SiO_2/100Fe$ catalyst had high WGS activity, even at 220°C. Since potassium promotes the WGS activity of iron Fischer-Tropsch catalysts (Figure 2), high WGS activity of these catalysts may be attributed to their high potassium content and lack of interaction between potassium and support. On the other hand, the observed decrease in the WGS activity with increasing amount of silica is an indication of partial neutralization of alkali promoter by acidic sites on silica, or decreased Fe/K contact due to the high catalyst surface area.

Hydrocarbon Product Distribution

Figure 10 illustrates the effects of support type and content and reaction temperature on hydrocarbon product distribution. For a given catalyst, reaction temperature did not have a marked effect on hydrocarbon selectivity. In most cases, the product distribution shifted toward lower molecular weight hydrocarbons (more methane and C_2-C_4 hydrocarbons, and less C_{12}+ products) with increase in temperature. The amount of liquid and solid (wax) products produced was high with all catalysts tested. This may be attributed to their high potassium content, since the latter favors production of high molecular weight products (Figure 3). All supported catalysts, except the $24SiO_2/100Fe$ catalyst, produced less methane and gaseous (C_2-C_4) hydrocarbons than the unsupported catalyst at all three reaction temperatures.

This trend is unexpected, since the promotional effect of potassium is expected to decrease with the addition of support. The expected trend was observed in a test with the $24SiO_2/100Fe$ catalyst, where the selectivity toward lower molecular weight products was greater than that obtained with the unsupported catalyst. With the $100SiO_2/100Fe$ catalyst one would expect to see even more methane and C_2-C_4 hydrocarbons, however, this catalyst produced less C_1-C_4 hydrocarbons than the unsupported one under all conditions tested. This suggests a possibility of some Fe-SiO_2 (metal/support) interactions, as a result of which there is an enhancement in selectivity of long chain hydrocarbons. This enhancement is large enough to compensate for reduction in surface basicity of the catalyst.

Olefin Selectivity

Figure 11 illustrates the effect of support (content and type) on total olefin selectivity, expressed as mass fraction of linear olefins of the same carbon number. The two alumina-supported catalysts and the $8SiO_2/100Fe$ had essentially the same olefin content as the unsupported catalyst, whereas the olefin contents for the catalysts containing 24 and 100 parts of SiO_2 per 100 parts of Fe were lower, particularly at higher carbon numbers. Potassium promotion supresses the olefin hydrogenation (Figure 4) which explains the high olefin selectivity (~80% for C_4-C_{15}) obtained in the test of the unsupported catalyst. In Figure 4, the maximum value of the olefin content in the C_4-C_{15} range was approximately 70%, and was obtained with a 100Fe/1K catalyst.

The data indicate that the interaction between potassium and alumina (or silica) support is minimal at low concentrations of the latter (up to 24 parts of support per 100 parts of iron), but it increases with increase in silica content. The olefin selectivity decreases with increase in silica content due to reduction in surface basicity of the catalyst, and/or decreased Fe/K contact due to high catalyst surface area.

Olefin Isomerization

Figure 12 illustrates the effect of support on 2-olefin selectivity as a function of carbon number. Results in the carbon number range 4-8 were omitted, as they showed erratic trends due to poor chromatographic separation between 1- and 2-alkenes during analysis. The addition of silica or alumina support in small quantities (8-24 g of support per 100 g of Fe) did not have an effect on selectivity of the unsupported catalyst. All these catalysts had low isomerization activity (2-5% of internal olefins) which did not vary with carbon number. This behavior is the result of the high level of potassium promotion and lack of interaction between potassium and support. The catalyst with the highest support content (100SiO_2/100Fe) had higher isomerization activity, and the 2-olefin selectivity increased markedly with carbon number, whereas the selectivity trends observed with the 24SiO_2/100Fe catalyst were between these two extremes.

Egiebor and Cooper (1985) also reported the increase in the internal olefin selectivity of hydrocarbons in the C_5-C_{11} range with increase in the silica content. Our results show that both secondary reactions, olefin hydrogenation and isomerization, increase with increasing silica content of the catalyst, which may be attributed to reduction in surface basicity due to reaction between potassium and silica. These trends are consistent with results obtained in studies on the effect of potassium promotion (Figures 4 and 5), where it was observed that both olefin hydrogenation and isomerization decrease with increase in potassium content of the catalyst.

Binder/Support Research - Conclusions

Addition of silica or alumina to the precipitated unsupported iron catalyst (100Fe/5Cu/4.2K) influences catalyst activity, stability, and selectivity during Fischer-Tropsch synthesis. Changes in catalyst performance become pronounced only at sufficiently high binder (support) concentrations and may be attributed to several factors: (1) changes in the catalyst texture (surface area and pore size distribution); (2) interactions between support and potassium and/or between metal and support.

The specific FTS activity decreased with increasing support content which may be ascribed to increased intraparticle diffusional resistance due to decrease in the average pore diameter, and lower degree of iron reduction following the catalyst pretreatment with CO. However, the catalyst stability improved with addition of silica either because of stabilization of iron crystallites during synthesis or due to a decrease in the carbon deposition rate resulting from partial neutralization of potassium promoter by acidic sites on silica (i.e. reduction in surface basicity). It was also found that the WGS activity decreased with increasing silica content of the catalyst (catalysts with 24 and 100 g of SiO_2 per 100 g of Fe). This is attributed to reduction in surface basicity and decreased Fe/K contact due to the high catalyst surface area.

Product selectivities also changed markedly with increasing silica content of the catalyst, whereas no significant changes were observed with the two alumina-containing catalysts. The total olefin content and the fraction of branched hydrocarbons both decreased, whereas the fraction of internal olefins increased with an increase in the silica content of the catalyst. These observations reflect the expected trends arising from the reduction of surface basicity of the catalyst with increasing silica content and are in agreement with results obtained in previous studies with similar catalysts (Dry, 1981; Egiebor and Cooper, 1985).

Hydrocarbon selectivities showed some unusual trends with increasing silica content of the catalyst. Catalysts containing 8 and 100 parts of SiO_2 per 100 parts of Fe produced less low molecular weight hydrocarbons (C_1-C_4) than the unsupported catalyst, whereas the catalyst containing 24 parts of SiO_2 produced more gaseous hydrocarbons. These results are indicative of complex metal-support interactions which require further investigation.

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Table 1 Effect of Promoters on Catalyst Activity and Selectivity at 250°C, 1.48 MPa, $H_2/CO=1$, $SV=2\ Nl/g-cat.h^a$.

Catalyst[b]	100/0/0		100/0/0.2		100/0/0.5		100/0/1.0	100/3/0		100/3/0.2			100/3/0.5		
Time on Stream (h)	72	144	72	168	72	168	95	73	167	72	143	429	72	143	456
H_2+CO Conversion (%)	21.4	21.8	30.9	37.8	40.2	53.8	44.4	57.3	60.6	76.0	78.1	76.8	75.9	78.3	69.6
CO Conversion (%)	21.3	22.4	37.1	45.0	50.5	61.9	55.0	65.9	70.8	89.3	91.3	90.2	91.0	93.8	83.9
Extent of WGS $\left(\frac{p_{CO_2}}{p_{H_2O}+p_{CO_2}}\right)$	0.41	0.48	0.94	0.95	0.88	0.92	0.96	0.79	0.91	0.89	0.93	0.92	0.93	0.91	0.99
$K_p = \frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}}$	0.83	1.17	24.7	27.2	35.9	43.4	52.5	7.50	11.7	34.2	54.2	35.8	49.2	63.4	80.3
HC Selectivities (wt %)															
CH_4	22.6	20.7	14.2	12.3	11.5	9.2	10.3	17.1	16.6	16.7	16.2	15.7	11.6	11.9	12.6
C_2-C_4	40.5	39.1	32.2	32.4	25.2	20.8	24.9	37.9	35.6	32.5	29.9	27.4	30.4	32.1	35.9
C_5-C_{11}	30.1	32.6	33.9	37.0	29.9	34.2	28.1	32.6	39.5	37.0	37.2	37.4	39.9	40.7	41.2
C_{12}+	6.8	7.6	19.7	18.3	33.4	35.8	36.7	12.4	8.3	13.8	16.7	19.5	18.1	15.3	10.3
CO Conversion to Products (%)															
Hydrocarbons	58.0	59.0	46.1	45.6	45.8	47.5	50.9	50.7	50.4	49.5	47.2	48.5	46.1	45.4	47.1
Oxygenates	5.5	4.5	2.7	3.0	2.7	2.3	3.4	2.1	2.3	2.5	2.1	1.8	4.4	5.1	4.5
	29.2	32.6	48.5	48.7	46.9	48.0	49.1	44.2	47.6	47.2	48.2	48.0	48.2	47.6	49.7
Unaccounted	7.3	3.9	2.7	2.7	4.6	2.2	-3.4	3.0	-0.3	0.8	2.5	1.7	1.3	1.9	-1.3
Olefin Selectivity															
C_2-C_4 (wt.%)	56.7	57.4	71.0	72.2	71.7	72.5	74.0	51.6	50.3	52.0	49.8	54.5	73.8	72.7	69.9
C_5-C_{11} (wt.%)	61.0	61.6	63.0	64.8	67.2	68.2	69.9	54.7	54.5	58.4	56.3	59.4	70.0	69.7	69.0
2-Butene/1-Butene	.23	.27	.15	.11	.03	.05	.06	52	.49	.19	.32	.54	.03	.03	.05

[a] Space velocity based on unreduced catalyst

[b] Catalyst composition given as parts by weight of Fe/Cu/K

Table II. Compositions and Properties of Synthesized Iron Catalysts

Nominal Composition (parts by weight)	Analyzed Composition (parts by weight)	Surface Area (m^2/g)*	Metal Exposure*
100Fe/5Cu/4.2K	100Fe/5.1Cu/4.1K	30	.015
100Fe/5Cu/4.2K/8SiO_2	100Fe/5.1Cu/4.0K/7.8SiO_2	95	.022
100Fe/5Cu/4.2K/24SiO_2	100Fe/5.4Cu/4.6K/28SiO_2	150	.021
100Fe/5Cu/4.2K/100SiO_2	100Fe/5.3Cu/4.1K/96.5SiO_2	250	-
100Fe/5Cu/4.2K/8Al_2O_3	100Fe/5.0Cu/3.9K/7.7Al_2O_3	85	.040
100Fe/5Cu/4.2K/25Al_2O_3	100Fe/5.1Cu/4.0K/20.5Al_2O_3	60	.0[illegible]1

* Following calcination in air at 300°C for 5 h and treatment in flowing CO for 4 h at 300°C.

Table III. Comparative Surface and Bulk Compositions of Supported Iron Catalysts*

Catalyst	Surface			Bulk
	Fraction of Fe^0	Fraction of Fe^{n+}	K/Fe	Fraction Reduced to Fe^0
100Fe/5Cu/4.2K	.85	.15	..	>.95
100Fe/5Cu/4.2K/8SiO_2	.60	.40	0.2	.75
100Fe/5Cu/4.2K/24SiO_2	.30	.70	<0.1	.25
100Fe/5Cu/4.2K/100SiO_2	.00	1.00	<0.1	<.10
100Fe/5Cu/4.2K/8Al_2O_3	.50	.50	0.2	.90
100Fe/5Cu/4.2K/24Al_2O_3	.40	.60	0.5	.60

* Following calcination in air at 300°C for 5 h, and treatment in flowing CO for 12 h at 300°C.

Table IV. Effect of Support on Catalyst Activity and Selectivity at 235°C, 1.5 MPa, $H_2/CO=1$, SV=2 nL/g-cat.h[a]

Catalyst[c]	unsupported		$8SiO_2$		$24SiO_2$		$100SiO_2$		$8Al_2O_3$		$24Al_2O_3$	
Time on Stream (*h*)	48	144	49	169	40	145[b]	41	143	41	144	48	144
CO Conversion (%)	93.6	54.7	93.8	52.9	59.6	50.1	24.4	20.1	90.3	50.8	82.2	37.1
H_2+CO Conversion (%)	78.3	47.2	76.7	44.8	55.0	48.7	29.1	25.7	75.1	42.9	68.3	31.5
Extent of WGS($p_{CO_2}/p_{CO_2}+p_{H_2O}$)	0.86	0.80	0.81	0.76	0.70	0.67	0.24	0.20	0.88	0.81	0.89	0.81
Hydrocarbon Selectivities (wt.%)												
CH_4	5.9	5.5	3.5	3.3	5.2	3.9	4.9	5.2	4.7	4.5	3.6	4.6
C_2-C_4	20.1	21.8	16.6	17.6	20.8	21.7	16.2	16.8	17.7	18.2	16.1	19.6
C_5-C_{11}	21.6	27.7	20.5	20.3	17.6	15.8	21.8	18.5	21.5	21.5	20.9	23.6
C_{12}+	52.5	45.0	59.4	58.9	56.4	58.6	57.2	59.5	56.2	55.8	59.4	52.3
CO Conversion to Products (%)												
Hydrocarbons	51.0	50.9	50.9	52.9	57.7	62.6	70.2	71.3	50.1	50.6	49.7	50.5
Oxygenates	2.5	3.0	2.7	2.4	2.2	2.4	4.5	5.1	2.3	2.6	2.1	2.1
CO_2	44.8	42.9	44.2	42.3	39.0	37.1	17.3	10.9	45.5	42.6	46.6	44.1
Unaccounted	1.7	3.3	2.2	2.4	1.2	-2.1	8.0	7.2	2.2	4.2	1.7	3.2
Olefin Selectivity												
C_2-C_4(wt%)	76.5	74.5	78.4	75.1	76.9	72.3	76.7	76.7	78.1	76.4	81.2	77.5
C_5-C_{11}(wt%)	79.0	78.5	77.9	77.6	77.7	77.3	74.8	76.1	78.2	78.3	78.4	78.8

[a] Space velocity based on unreduced catalyst

[b] SV=4 nL/g-cat.h, P=3.0 MPa

[c] Active metal and promoter amounts for all catalysts: 100 Fe/5 Cu/4.2 K (in parts by weight)

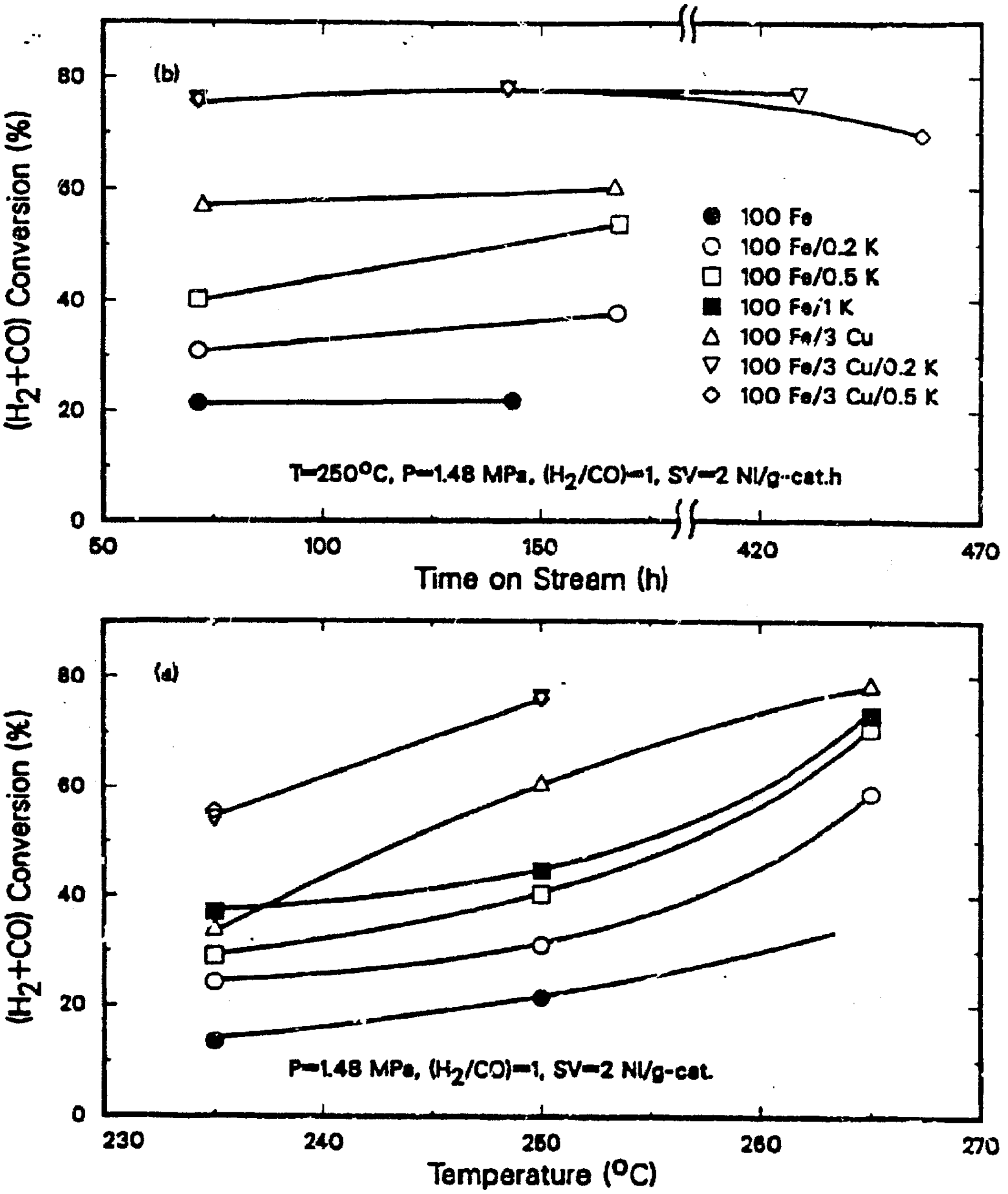


Figure 1. Promoter effects on catalyst activity and stability, (a) (H_2+CO) Conversion vs. reaction temperature, and (b) (H_2+CO) Conversion vs. time on stream at 250 °C.

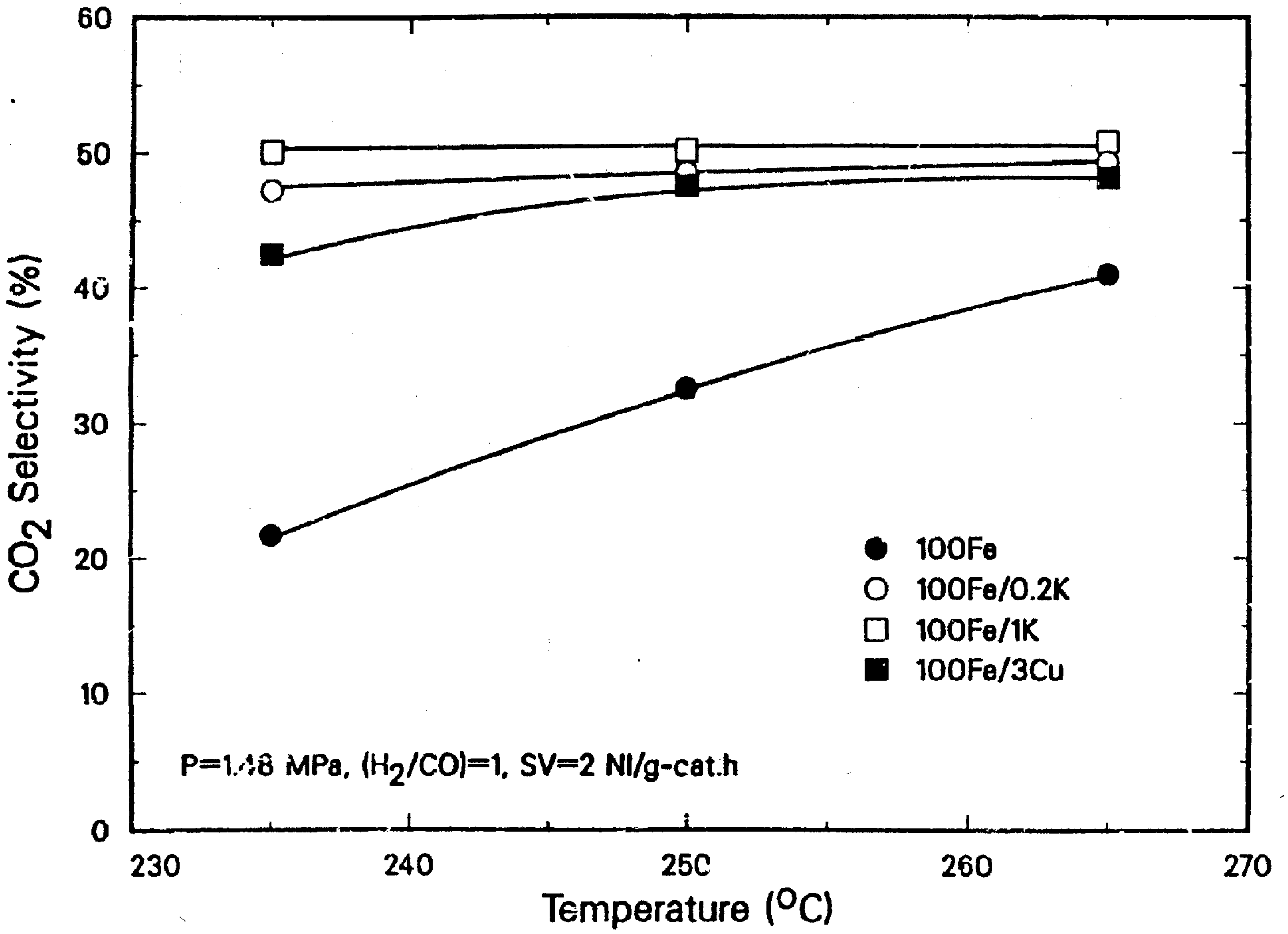


Figure 2. Effect of promoters and temperature on Water-gas-shift activity.

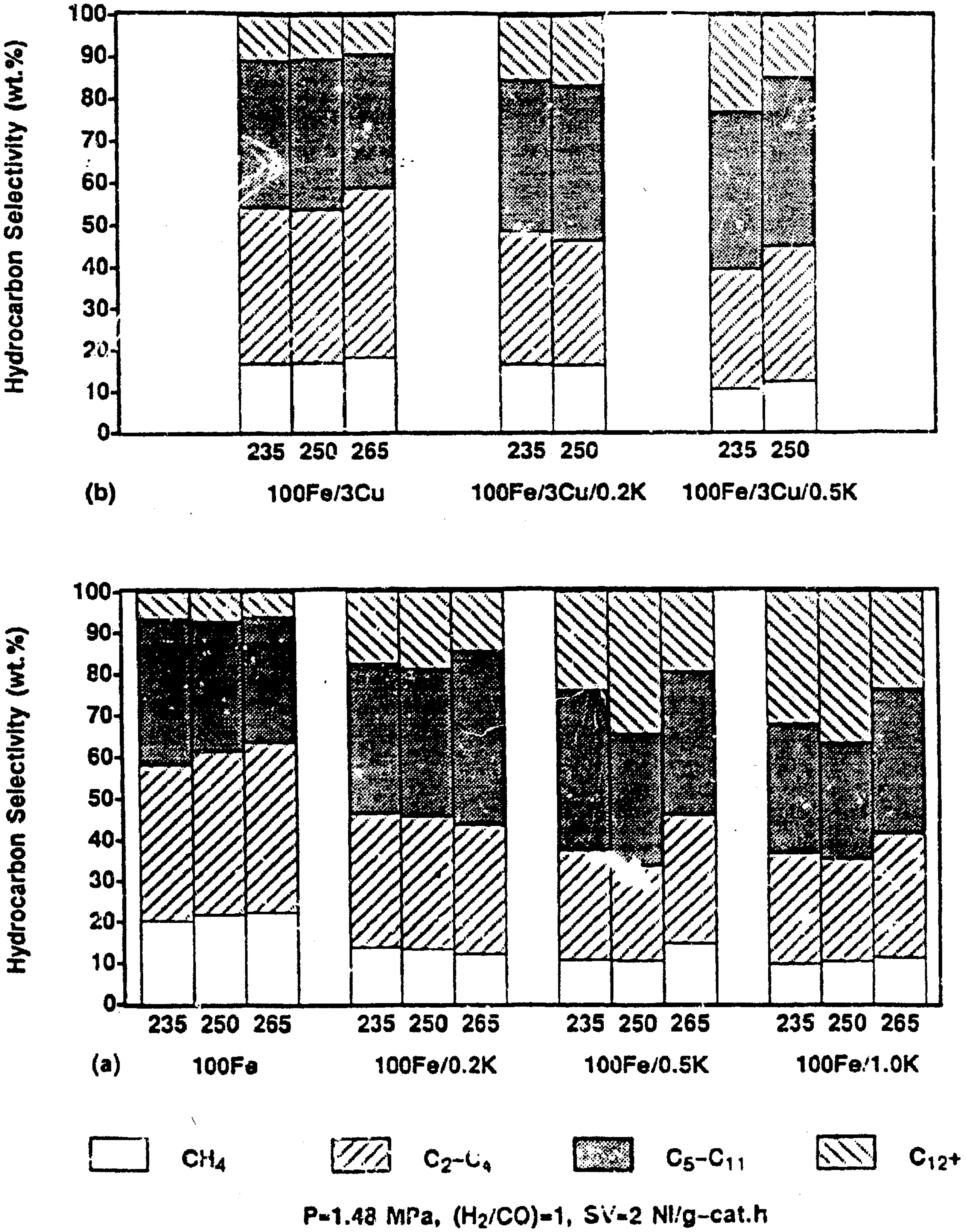


Figure 3. Effect of potassium content and reaction temperature on hydrocarbon selectivity for (a) singly promoted Fe/K catalysts, and (b) doubly promoted Fe/Cu/K catalysts.

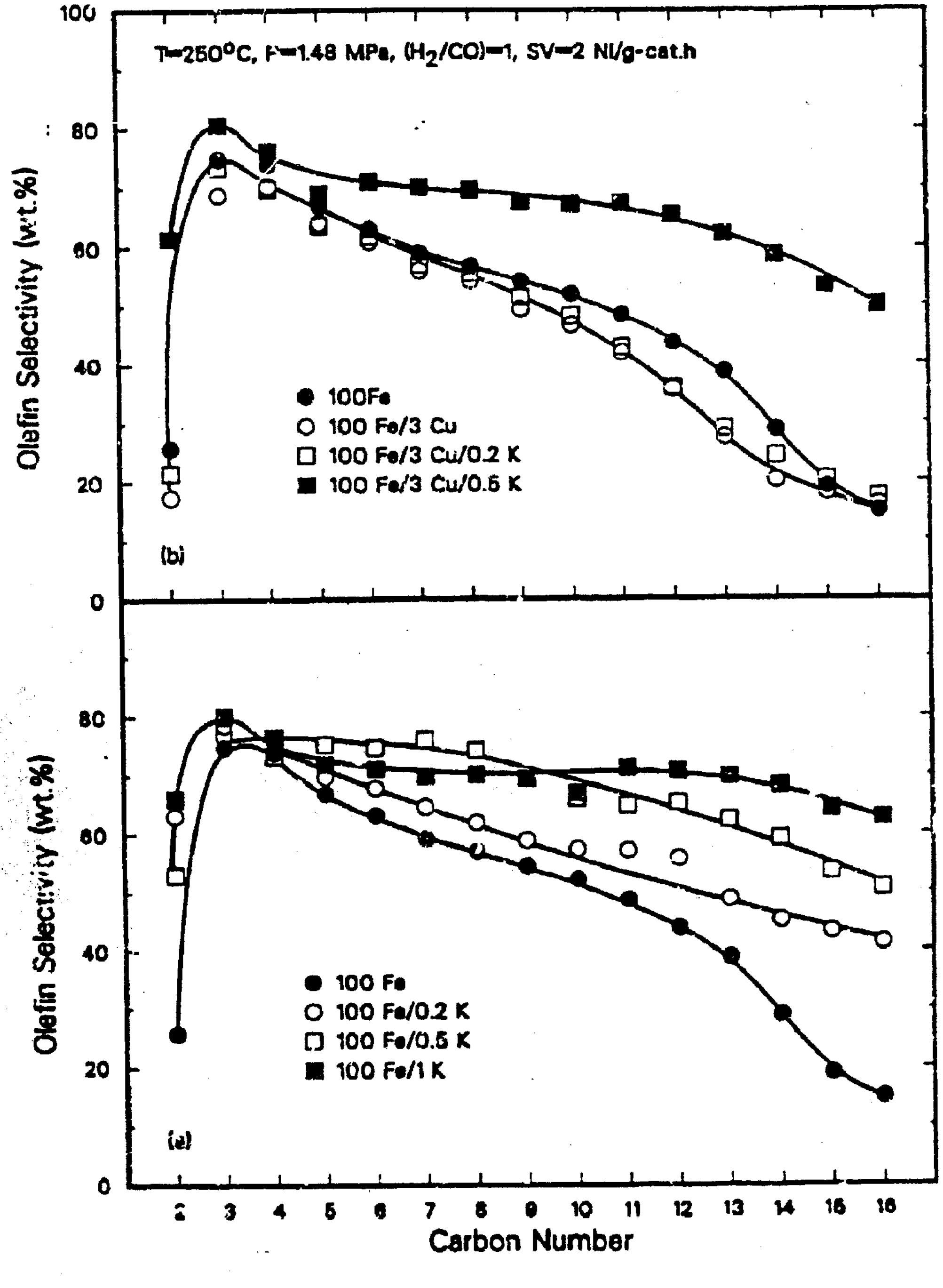


Figure 4. Effect of potassium content on olefin selectivity for (a) singly promoted Fe/K catalysts, (b) doubly promoted Fe/Cu/K catalysts, and comparison with results for unpromoted iron.

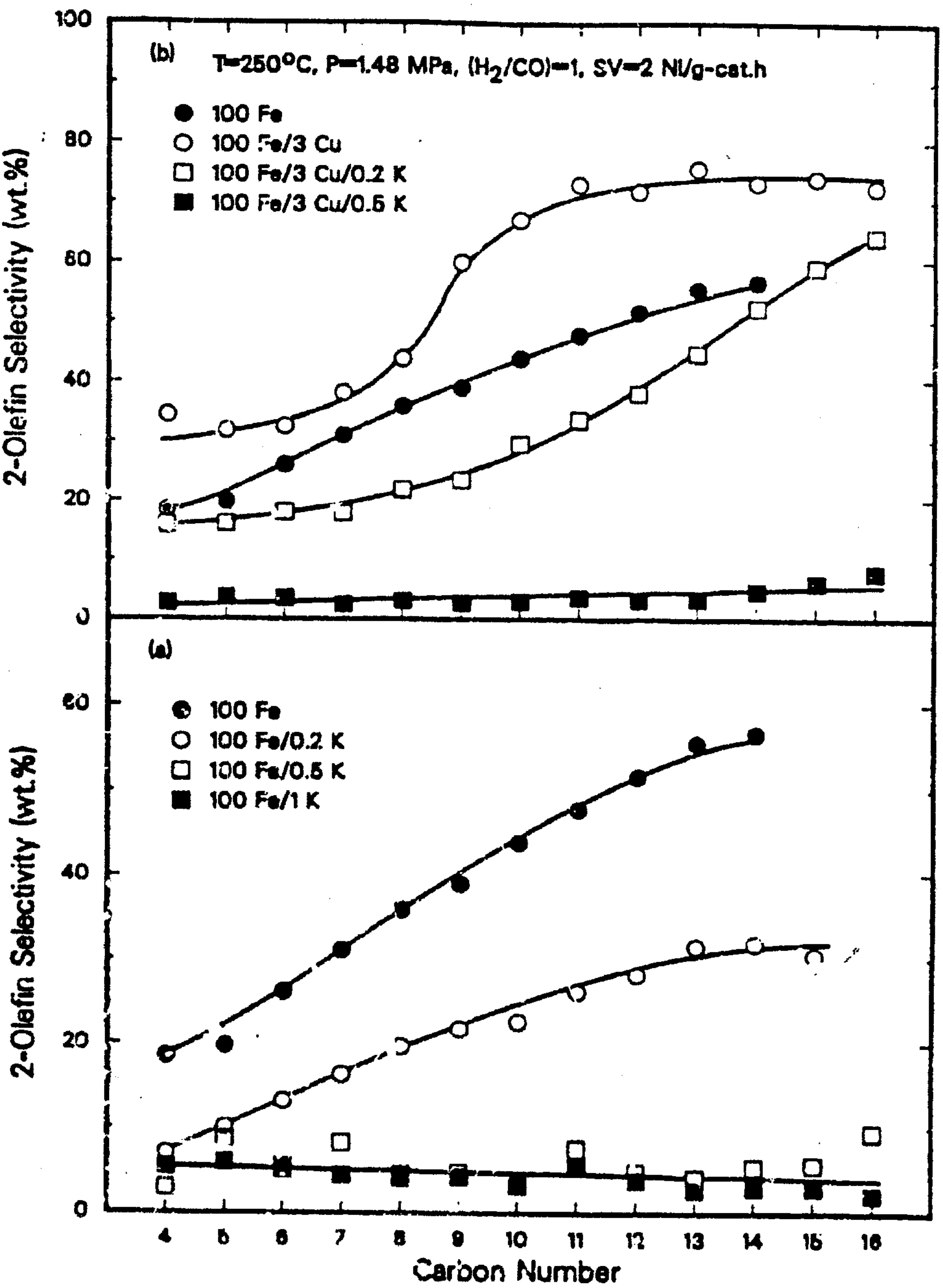


Figure 5. Effect of potassium content on 2–olefin selectivity for (a) singly promoted Fe/K catalysts, (b) doubly promoted Fe/Cu/K catalysts, and comparison with results for unpromoted iron.

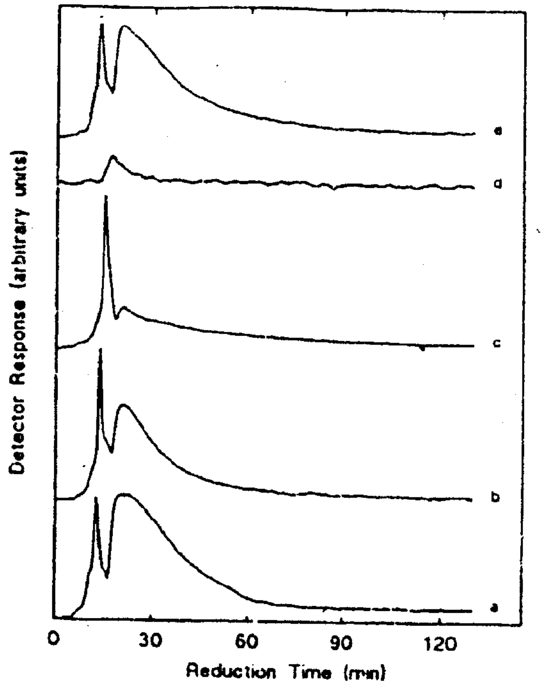


Figure 6. Programmed/isothermal reduction profiles in CO at 300°C of: 100 Fe/5 Cu/4.2 K: (b) 100 Fe/5 Cu/4.2 K/8 SiO_2; (c) 100 Fe/5 Cu/4.2 K/24 SiO_2; (d) 100 Fe/5 Cu/4.2 K/100 SiO_2; (e) 100 Fe/5 Cu/4.2 K/8 Al_2O_3.

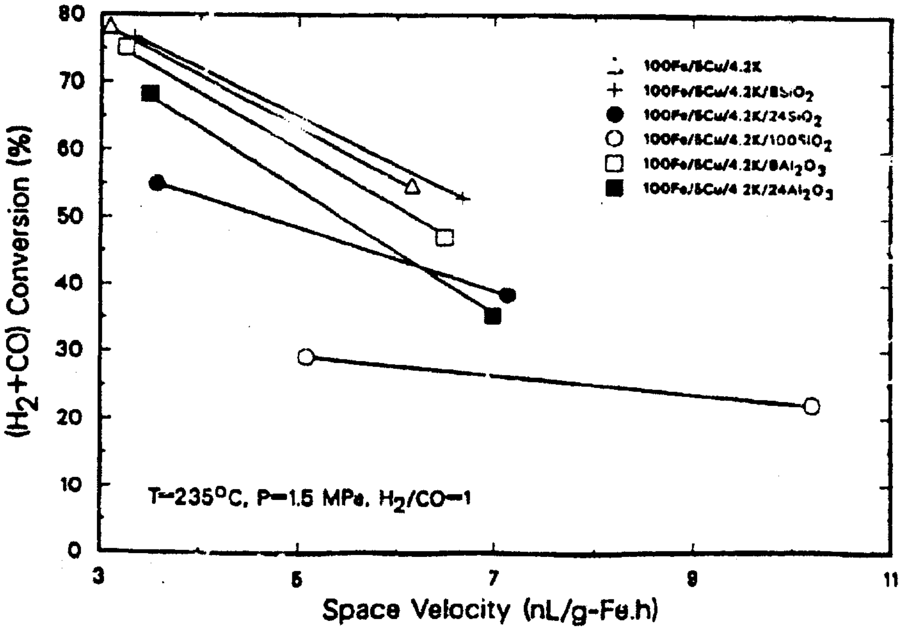


Figure 7. Effect of catalyst support and gas space velocity on Fischer-Tropsch activity.

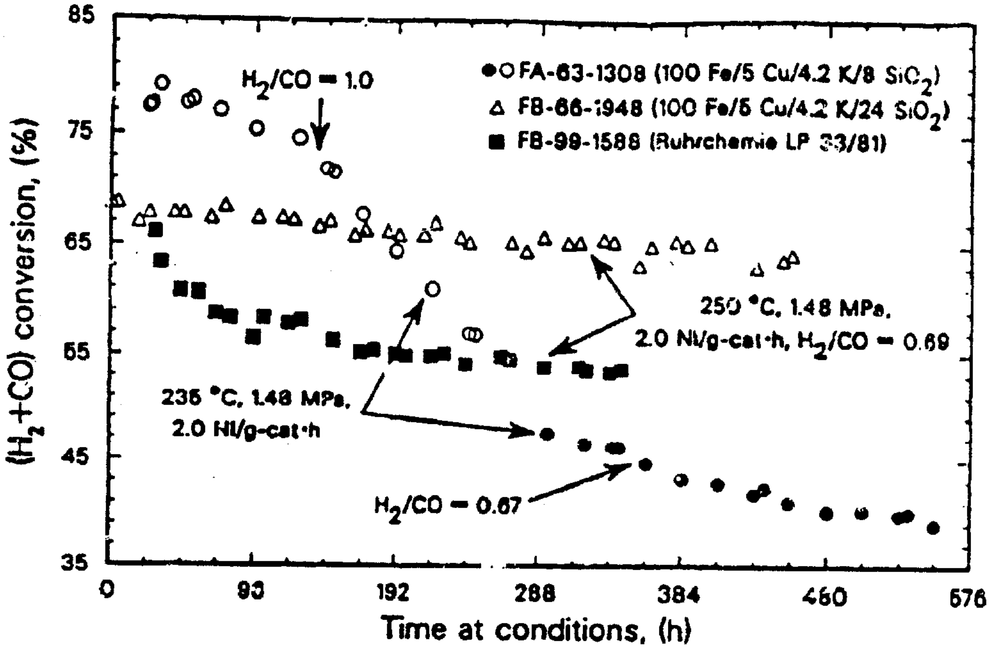


Figure 8. Comparison of activity and stability of iron/silica catalysts (Fixed bed tests).

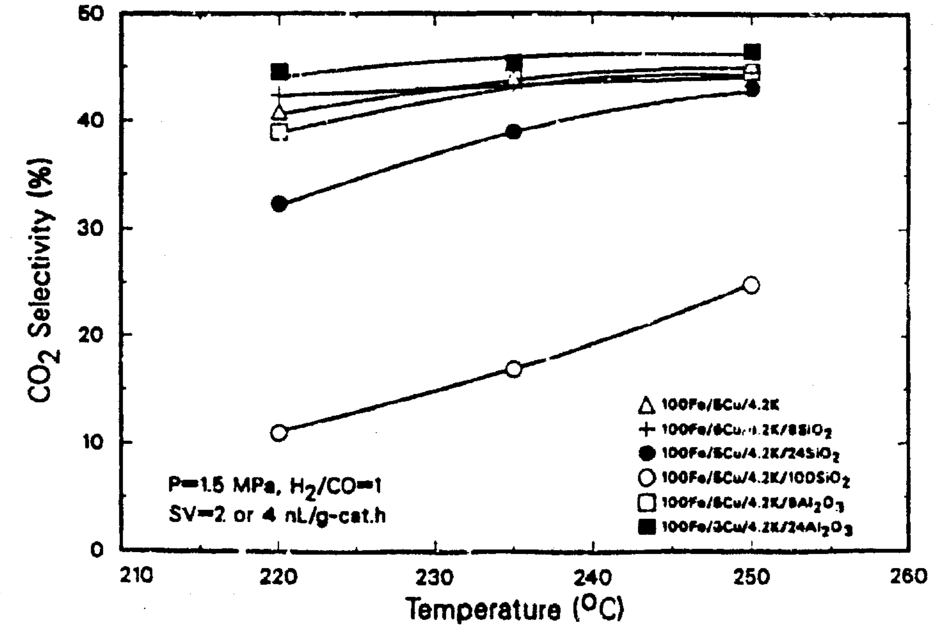
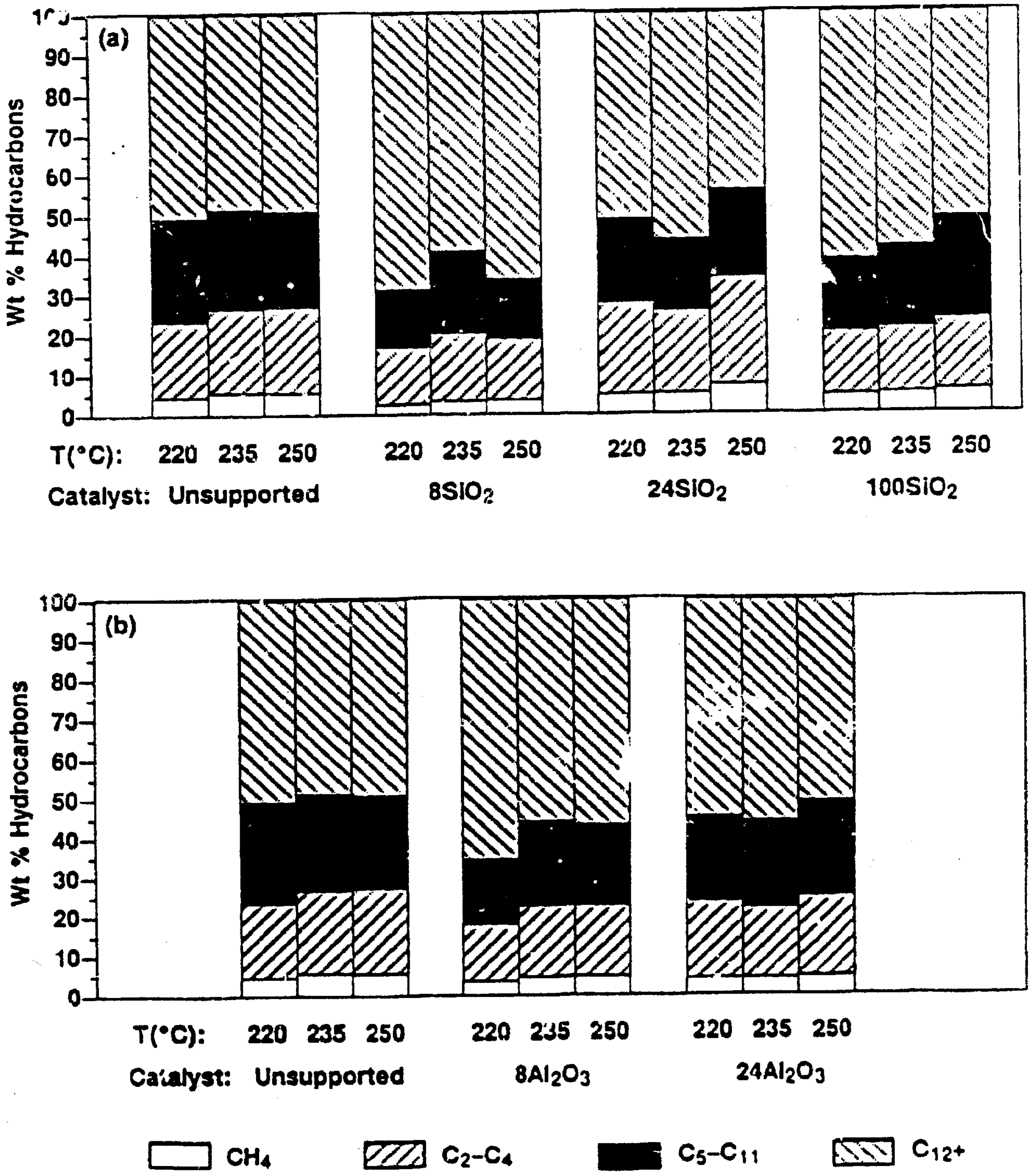


Figure 9. Effect of catalyst support and reaction temperature on water-gas-shift activity.



$P = 1.5$ MPa, $SV = 2$ or 4 nL/g-cat.h, $H_2/CO = 1$

Figure 10. Effect of support type and content, and reaction temperature on hydrocarbon selectivity (a) silica-supported catalysts, (b) alumina-supported catalysts.

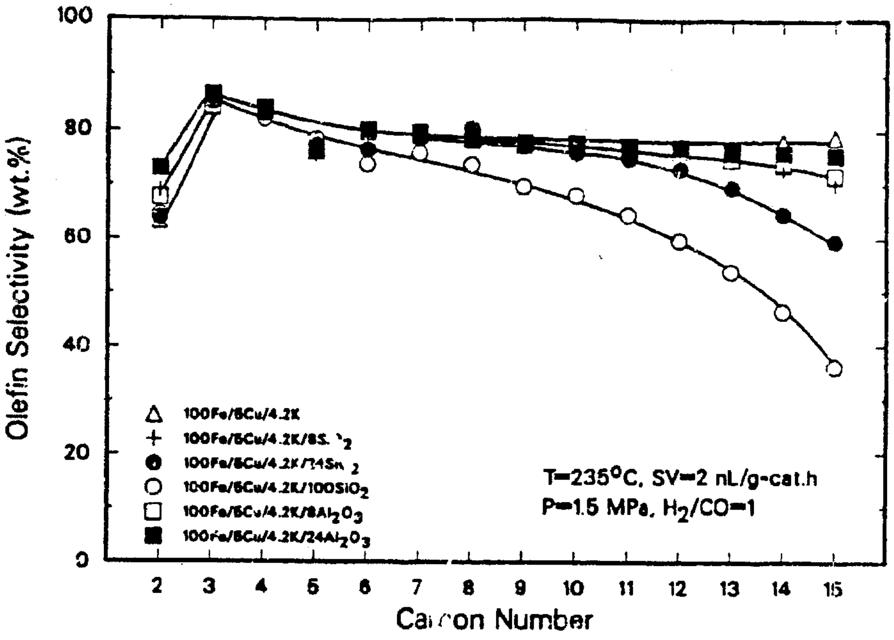


Figure 11. Effect of support type and content on olefin selectivity.

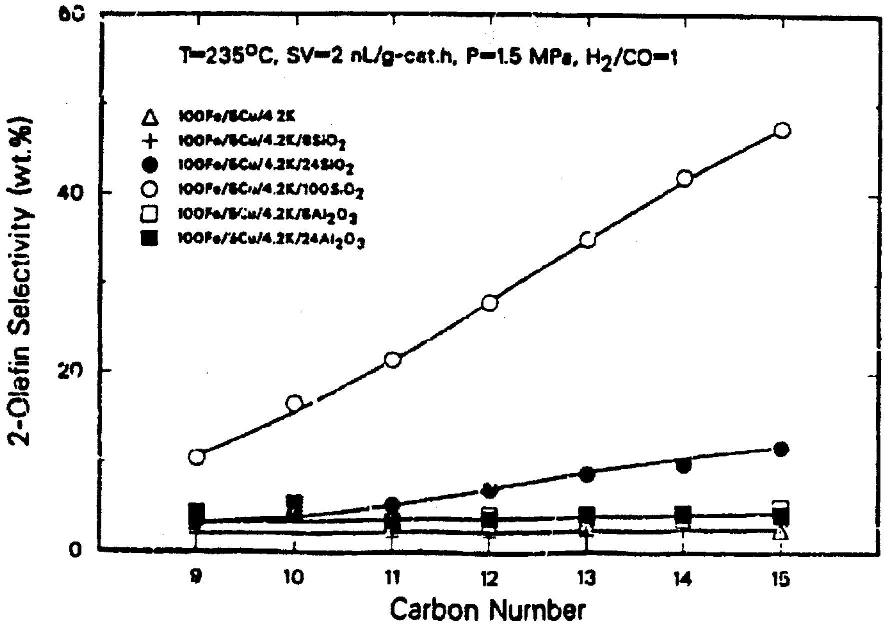


Figure 12. Effect of support type and content on 2-olefin selectivity.