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Fischer-Tropsch synthesis: relationship between iron catalyst composition and process variables

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Abstract

The work at the CAER has focused on the development of a family of iron catalysts with different alpha values with the objective of providing the option of producing a broad slate of fuel and chemical products. To make a valid comparison of iron and cobalt catalysts with respect to activity and selectivity, the conversions with the iron catalysts have been carried out over wide ranges of operating conditions including pressure, temperature, H_2/CO ratios, diluent gases (both inert and reactive) and conversion levels. As an approach to define the extent of secondary reactions in determining the products that are produced, a variety of isotopically labeled olefins, alcohols and carbon dioxide have been utilized. The extent of incorporation of these compounds can be defined by determining the isotopic distribution in the products. Catalyst samples, withdrawn from the reactor during synthesis, have been characterized to define changes that occur during catalyst use.

Keywords: Iron catalyst; Fischer-Tropsch synthesis; Process conditions; Mechanism; Isotopic tracers

1. Introduction

The Fischer-Tropsch synthesis (FTS) to convert carbon containing feedstocks to transportation fuels and petrochemical substitutes has been utilized for more than 75 years. FTS involves three process steps: (1) the generation of the synthesis gas, a mixture of CO and H_2; (2) the conversion of the syngas to a mixture of hydrocarbon and oxygenate products; (3) hydroprocessing of synthesis products to produce transportation fuel products, today with emphasis on diesel.

A number of approaches are available for the conversion of synthesis gas. Two catalysts—iron and cobalt based—have been widely used and these are the only ones receiving serious consideration today. The major difference between the two catalyst types is the formation of the oxygen containing product: with cobalt the oxygen in the syngas is rejected as water and with iron the oxygen is rejected as carbon dioxide. Since cobalt catalysts do not have water-gas-shift (WGS) activity, the feed gas must have a H_2/CO ratio of about 2.0–2.3. Iron based catalysts have significant WGS activity so that much lower H_2/CO ratio feed gas can be utilized. Thus, the perception has developed that the iron catalyst is preferable for syngas with a low (0.5–1.3) H_2/CO ratio, typical of those produced from coal as the carbon source, and that the cobalt based catalyst is preferred for high (2.0+) H_2/CO ratios, typical of those produced from natural gas. Since natural gas usage is the primary driving force for FTS today, cobalt has been receiving much attention. However, the following indicates that iron catalysts should not be automatically eliminated from consideration for syngas derived from natural gas.

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2. Catalyst preparation

The early work on FTS was done using fixed-bed reactors. This dictates that the particle size of the catalyst to be sufficiently large so that significant pressure differences across the catalyst bed did not develop and that the catalyst particle had sufficient strength to survive months of usage in the reactor. In the early industrial development and commercialization work, cobalt catalysts were utilized. These physical properties were not important considerations for the cobalt catalyst since the properties of robustness could be imparted by the use of those of the catalyst support. However, for the iron catalyst the need for these properties led to the use of sintered, lower surface area materials. In fact, much of the early work was conducted with an iron catalyst that was, or resembled, the fused-iron Ammonia synthesis catalysts. When precipitated catalysts were used, sintering at reasonably high temperatures and/or the incorporation of a binder was utilized.

The first large scale use of iron catalysts was accomplished during the 1940–1950s in plants utilizing fluidized bed reactors. A plant located at Brownsville, TX utilized a fixed-fluid bed reactor while circulating fluidized bed reactors were used later by Sasol. In both instances the fluidization and circulation of the catalyst particles demanded great strength to ensure physical integrity during the use of the catalyst. Because of the catalyst inventory and the significant loss by attrition, a low-cost source of catalyst precursor was needed. Thus, Sasol settled upon the use of mill-scale from iron manufacturing plants as the base material and modified it by the addition of suitable promoters. The operation of these fluid bed reactors required the use of catalysts with low alpha values to ensure that the products were in the gas phase at the reaction temperature. The formation of significant amounts of liquid products would "wet" the catalyst particles, leading to agglomeration to produce particles too large to remain fluidized.

While particle agglomeration was a problem in fluid bed operations, the disintegration of the catalyst particles due to carbon formation was the major problem to overcome. At the high temperatures needed to obtain sufficient catalytic activity with the low surface area materials, the conditions needed for carbon filament growth were present. The formation of carbon filaments led to two problems. First, the density of the catalyst particle changed as carbon was incorporated and this led to problems of keeping the particle in the fluid bed. The other problem was that the growth of carbon introduced stresses within the particle, leading to breakup of the particle to produce much smaller particles which did not remain in the catalyst bed. Sasol personnel were able to develop operating measures that permitted them to control carbon fiber formation to manageable levels. Nevertheless, the severity of the problem and the publicity associated with developing control measures ensured that carbon formation became ingrained as a major problem associated with the use of iron catalysts. This view survives today even though it has been reduced to manageable levels for high-temperature operations and is not a problem for low-temperature operations.

More recently, liquid phase synthesis has become preferred so that smaller particle sized catalysts are desirable. The early work in the liquid phase was with low activity catalysts. Two general approaches for reactor design were utilized [1]. For one approach the catalyst was stationary on trays and liquid was passed over the catalyst. In the other, the large catalyst particles were kept in suspension by a combination of liquid and gas flows.

The early liquid phase synthesis work at the US Bureau of Mines was conducted with fused-iron catalysts operated in an ebullated bed reactor where the intermediate boiling products were recirculated to help remove heat and to provide suspension of the catalyst [2].

The availability of more active catalysts has led to the use of smaller particle sizes and these normally are in the range of 30–100 μm. These particles can be suspended rather uniformly within the reactor by the upward flow of the gas. Today a high surface area precipitated iron catalyst precursor is employed [3]. At CAER, iron nitrate and colloidal silica as one feed-stream and ammonium hydroxide as the other are fed to a continuous stirred tank reactor, and materials that have a surface area of about 300 m^2/g are readily produced. Calcination of these materials result in significant loss of surface area. The loss of area with temperature is more rapid than a linear relationship; thus, calcination at a temperature of 350 °C leads to a surface area in the range of 50 m^2/g or less. The initial surface area, as well as the loss of surface area, depends upon the amount and type of silica, or other additive, incorporated into the precipitated material. In general, the incorporation of silica or alumina results in a rapid increase in surface area, following calcination, with additive up to a level of about 6–10 wt.% and then a nearly constant area with the incorporation of more additive.

Two metals are normally present in the iron catalysts, these are potassium and copper. The materials have been incorporated by impregnation of the iron precipitate with an aqueous solution of the appropriate salts. Potassium impacts both the activity and the product selectivity of the catalyst, as described below. The impact of copper significantly impacts how rapidly the catalyst attains the maximum activity but controversy still surrounds its impact on other catalyst properties.

Spray drying of the slurry of precipitated catalyst precursor is a common approach to obtain catalyst particles of the desired size range.

More complex synthesis procedures have been applied to prepare unsupported iron catalysts. For example, Rice et al. [4,5] utilized a laser to induce iron carbonyl present in a stream of ethene to react to produce iron carbide catalysts. One advantage of this approach is that the product could be produced so that one, or nearly one, iron carbide phase is present. While this is an elegant method to prepare a catalyst, it would be difficult to scale the approach to a commercial level to produce catalysts at a price that is competitive with precipitation approaches. Furthermore, we have found, at least for an unpromoted catalyst prepared using this approach, that phase changes occur rapidly so that the initial advantage of the catalyst composition is partly, or completely, lost in a few hundred hours of synthesis [6]. In another approach, Soled et al. [7] utilized a strong reducing agent such as calcium metal to completely reduce mixed metal iron oxides to form alloys. This approach allowed the alloy to be prepared at a lower temperature than the conventional melt technique. Again, the cost of the finished catalyst when scaled to commercial operations could limit the use of this method. Another approach to prepare high surface area iron oxide is the pyrolysis of a suitable compound; one that has been used to produce commercial quantities of iron oxide is pyrolysis of iron carbonyl. The surface area of the material is about 300 m^2/g and the particle radius is about 3 μm; the cost was about US$ 800/kg. While the material produced in this manner consists of individual particles that are easily dispersed, the surface area and particle diameter is in the range that is obtained by a common precipitation technique. Furthermore, it has been shown that these small particles grow during FTS so that at least some of the initial advantage is lost [8,9]. A final example is the preparation of a metal spinel [10] such as $Fe_{3-x}Zn_xO_4$ (x such that Fe/Zn $\geq$5) that involves a preparation technique that included the mixing of a solution of iron and zinc nitrate with an ammonium glycolate solution to provide a preselected pH value; the resulting mixture evolved significant amounts of gas and expanded the catalyst mass to a large volume [11]. After calcination, the catalyst precursor was impregnated with promoters. Again, the volume expansion makes it questionable whether this method could be scaled for commercial operations. Thus, while there are many approaches for the preparation of high surface area iron oxides, for commercial considerations it will be a demanding task to find one which is superior to a precipitation procedure.

3. Catalyst activation

There are three general approaches that can be employed for catalyst activation of an iron catalyst and these utilize: (1) CO, (2) H_2, or (3) syngas. Two situations are encountered: laboratory/small pilot plant and commercial scale operations. To develop catalysts for commercial scale operations, it is necessary to conduct lengthy optimization studies to develop the most suitable approach to activate the catalyst to produce high activity and long catalyst lifetime. At the laboratory scale, it is desirable to have a simple and reliable approach that does not require one to do many runs to define the optimum conditions for each catalyst to be tested. We have found that activation in CO at 270 °C for 24 h will provide the maximum, or very near the maximum, conversion that can be obtained by other activation procedures. Thus, for scanning a variety of catalysts in the laboratory, this activation can be used without resorting to learning the optimum temperature ramp protocol. Since a commercial facility would generally not have a ready source of pure CO, activation with this gas should be viewed to be an approach to optimize experimental work at the laboratory scale.

In general, the catalyst precursor is treated with the gas initially at conditions that differ from those used for the synthesis. For example, the US Bureau

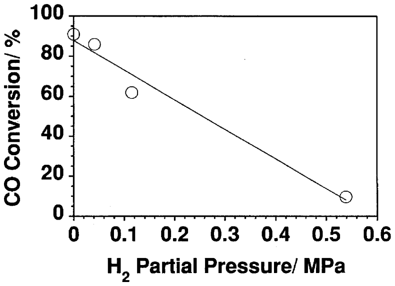

Fig. 1. CO conversion following activation with a syngas containing various partial pressures of H_2 (catalyst: 100 Fe/3.6 Si/0.7 K; FTS conditions: 270 °C, 1.31 MPa, H_2:CO: 0.7:3.1 NL h^{-1} g per Fe).

of Mines workers utilized a temperature ramp in syngas that would produce about 20% CO_2 in the exit gas; this procedure could take several days, or even weeks, until the maximum conversion was attained. Others have utilized treatment of the catalyst precursor in syngas at temperatures about 20 °C higher than utilized for the synthesis. In general, the activation in syngas leads to a catalyst with lower activity than one activated in CO, as shown in Fig. 1. The data in Fig. 1 are for a catalyst that does not contain copper and it has been found repeatedly that a catalyst with little activity is obtained when the activation has even a low H_2/CO ratio of about 0.7, as is typical of a syngas derived from coal. The activation is improved by the presence of copper but even here a low activity is obtained initially and there is a long induction period (100 h or longer) during which the CO conversion increases gradually. Thus, while activation by syngas may be highly desirable since a common gas supply can be used for activation and synthesis, it generally requires a very specific protocol.

Sasol utilizes an activation in H_2 prior to introducing the material into the reactor at synthesis conditions [3]. Small amounts of copper are usually incorporated into the catalyst to catalyze the reduction. Both the catalyst precursors, Fe_2O_3 and Fe_3O_4, are prone to sintering at elevated temperatures. Sintering of metallic iron likewise occurs at elevated temperatures. Thus, copper is beneficial since the reduction to first Fe_3O_4 and then to elemental Fe can be accomplished at one to two hundred degrees lower temperature than is possible when copper or some other easily reduced metal oxide is not present. We have found that partial reduction of a high surface area iron oxide precursor is preferred to complete reduction to metallic iron since, in general, a higher ultimate surface area is obtained from the material that is incompletely reduced in hydrogen. However, when the catalyst precursor is the low-area fused iron or iron oxide, complete reduction to the metal appears to be required to provide a catalyst with the highest activity obtainable from the precursor.

Another approach is to prepare the carbide form of the catalyst ex situ and then transfer the material to the reactor. Emmett and coworkers [12] heated an iron oxide in a flow of hydrocarbons and obtained iron carbides of reasonable surface areas. Another approach is to convert the oxide to an intermediate compound which is then converted to the carbide. Procedures have been developed that permit the oxide to be converted to a high surface area nitride and then to convert the nitride to the carbide by heating in a flow of a suitable hydrocarbon [13]. To date this method has been found to be more useful for metals that are not good FTS catalysts.

It is not necessary that an active iron catalyst have the carbide phase. Anderson [14] made extensive use of iron nitrides as FTS catalysts. However, [15] it has been shown that the nitride is not stable under typical FTS conditions and that the nitride gradually converts to carbide phases. It therefore is likely that the surface nitride layer converts to a carbide form during the initial synthesis period.

4. Catalyst induction

The iron catalyst is seldom, if ever, at its maximum activity following the activation step. Thus, during some period of time, the activity and at least some of the selectivities, will change with time-on-stream. The length and extent of the activity change depends upon the catalyst composition and the reaction conditions. In general, the induction period is longer at lower temperature conditions and it is also longer for catalysts with higher alkali content, as shown in Fig. 2. During the time period when the CO conversion was increasing and then decreasing to a stable level, the hydrocarbon fraction represented by methane decreased gradually to attain a steady state after about 200 h rather than exhibiting a minimum value followed by an increase to the steady state. The alkene

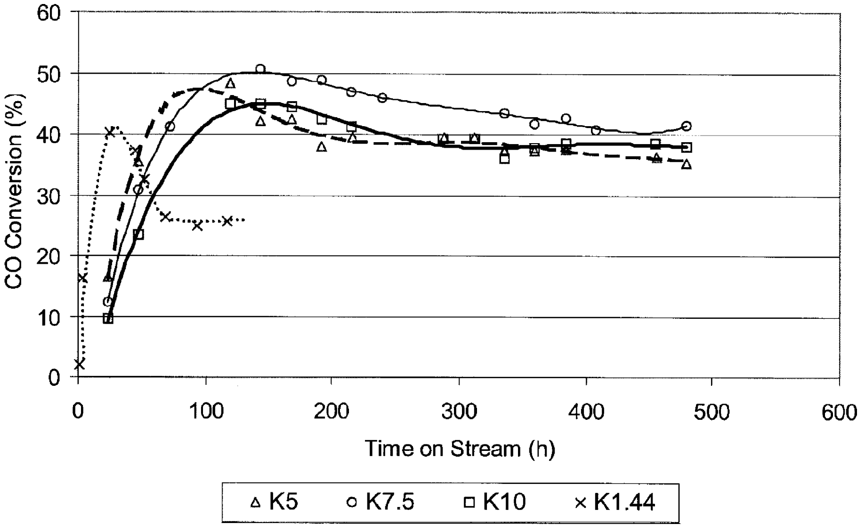

Fig. 2. Potassium effect on induction period and CO conversion.

selectivity for the C_2–C_4 fraction increased during the induction period, showing a decreasing trend in hydrogenation activity that parallels the decrease in methane selectivity. The WGS activity of the catalyst increases during the induction period and attains a steady state value in less than 100 h of synthesis. Thus, there is some change in the catalyst during the induction period that causes the selectivity to show lower hydrogenation activity at the same time that WGS activity increases to produce a higher H_2/CO ratio. These trends are contrary to the anticipated changes.

Since the activity and product selectivities are changing during the induction period, it is reasonable to expect that the chemical composition of the catalyst is undergoing changes. Samples of the catalyst containing K:Fe = 0.05:100 were withdrawn at intervals from the reactor as synthesis time increased during the early period of synthesis (until the maximum conversion was obtained). Mössbauer data indicated that the sample underwent at most a slight change during the dramatic changes in activity and selectivity during the induction period. After the 24 h activation the catalyst was essentially the carbide phase and remained this phase as the activity and selectivity changed [16]. Thus, the bulk composition is not a dominant factor in determining the selectivity and activity of this catalyst, and, presumably, not the other catalysts shown in Fig. 2.

5. Flow rate (conversion level)

The productivity of an iron catalyst depends strongly on the conversion level. A typical productivity curve is illustrated in Fig. 3. In addition to the productivity, the fraction of CO that is converted to hydrocarbons decreases as the CO conversion increases (Fig. 4). Because of this productivity and selectivity dependence on conversion, we have proposed utilizing reactors in series, preferably operating each reactor so that the H_2/CO ratio of the exit gas is the same as the feed [17]. Thus, two advantages accrue when operating an iron catalyst at lower ($\lesssim$ 50%) conversion levels: (1) the catalyst provides a higher CO conversion per unit weight of Fe and (2) a higher fraction of CO converted goes to desirable hydrocarbon products rather than to producing excess hydrogen and CO_2.

6. H_2/CO ratio

The conversion of CO does not show a strong dependence upon the H_2/CO ratio over the range of 0.7–1.7 (Fig. 5). The H_2 conversion, because of the WGS reaction that produces H_2, shows a dependence on the H_2/CO ratio. Product selectivity shows the expected dependence upon the H_2/CO ratio, with unsaturates being lower at high ratios, but this is not a strong

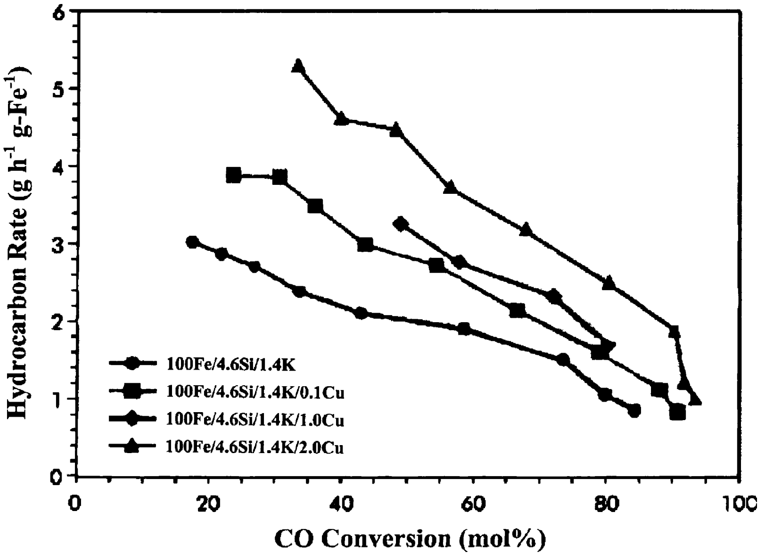

Fig. 3. Hydrocarbon rate at various conversion levels with low alpha catalyst operated at 270 °C.

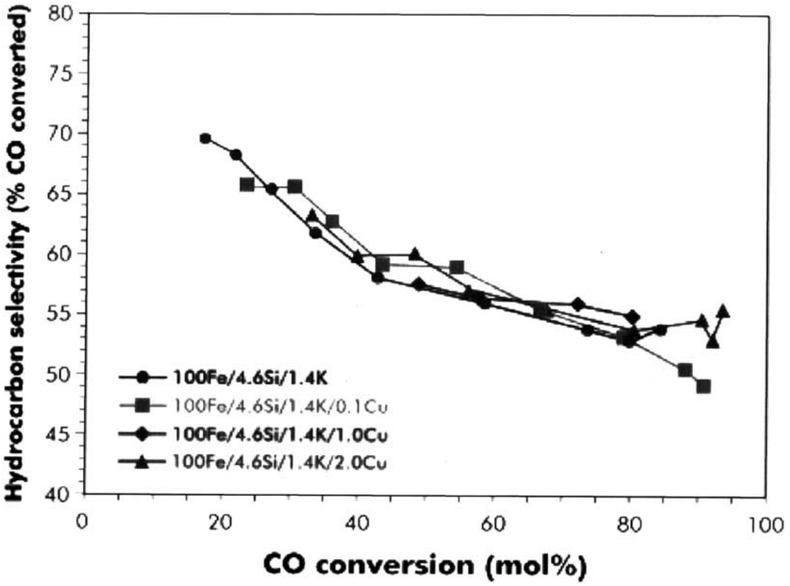

Fig. 4. Fraction of CO converted to hydrocarbon with increasing CO conversion.

dependence (5% difference in olefin/paraffin ratio or less for C_3 and higher carbon numbers). Thus, for the range of H_2/CO from 0.7 to 1.7, there is, at most, a slight dependence of catalytic activity and product selectivity on the H_2/CO ratio.

7. Water product

The iron catalyst has appreciable activity for the WGS reaction. For high-temperature operations, the WGS is essentially at equilibrium and this determines

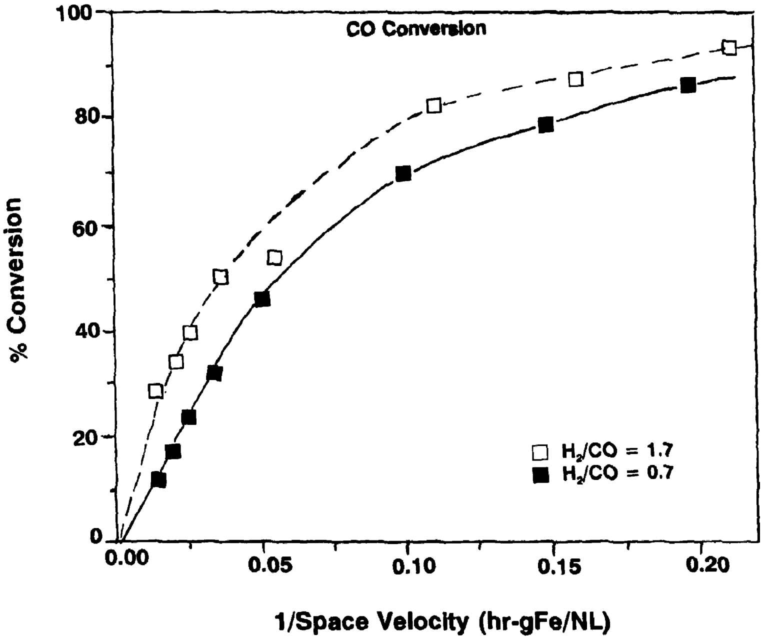

Fig. 5. Comparison of CO conversion with time for $H_2/CO = 0.7$ and $H_2/CO = 1.7$ (270 °C and 1.16 MPa).

the partial pressure of water. This is not the case for low temperature conditions. At lower CO conversion levels, the partial pressure is low so that WGS is low. As the partial pressure of water increases, the rate of WGS increases up to about 50% CO conversion (Fig. 6). At this conversion level, the H_2 partial pressure is low enough so that the FTS rate becomes dependent upon the production of H_2 by the WGS reaction. Thus, above about 50% CO conversion, the WGS reaction becomes rate controlling. The partial

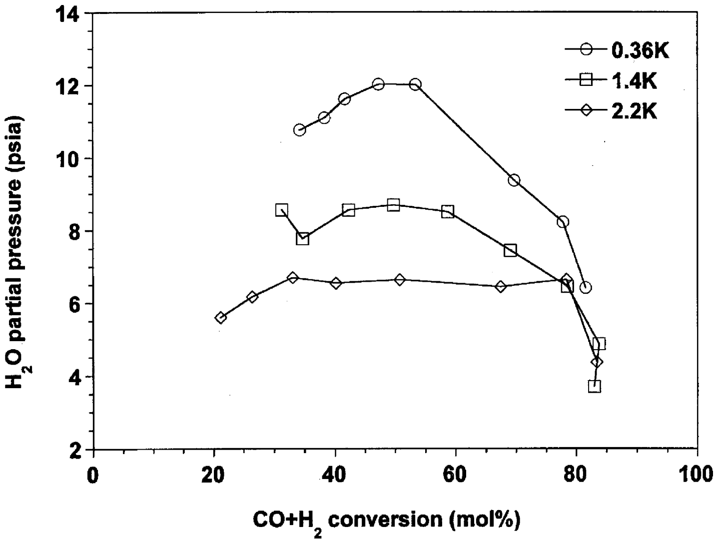

Fig. 6. Water partial pressure in the reactor at various conversion levels for catalysts with different K content.

pressure of water increases with CO conversion to attain a maximum value at about 50% CO conversion.

The presence of water in the feed has little impact upon the FTS at low concentration levels. However, when the H_2O/CO levels in the feed reach a high level (significantly greater than one), the conditions are sufficiently oxidizing that the catalyst loses essentially all of its activity for FTS.

It would be desirable to have the beneficial impact of the potassium promoter without having the detrimental impact of it on the WGS activity. To examine this, a series of alkali [18] and alkali-earth [19] promoted catalysts were prepared and evaluated for their relative activity and WGS/FTS selectivity. While there was some indication of producing a lower WGS/FTS activity ratio with some of the promoters, at this time the data indicate that the benefit that can be expected at reasonable CO conversion levels is marginal.

8. Temperature

The first utilization of iron FTS catalysts in a commercial operation was at the Brownsville, TX plant; however, this operation was terminated just as most of the operational problems were solved [20]. Thus, the Sasol plants were the first to utilize the iron catalyst in major commercial operations. Most of the production at the Sasol plants comes from the use of the circulating fluidized bed reactors, and now the fixed-fluidized bed reactors [21]. Because the fluidized bed reactors could only be operated when the products were in the gaseous phase, it was necessary to utilize high temperatures and low alpha catalysts. Under these conditions, the majority of the products were in the light (C_1–C_4) gas and gasoline (C_5–C_{11}) range. At these conditions, the WGS reaction maintained a nearly equilibrium mixture of CO and CO_2 as well as H_2 and H_2O. Much of the knowledge of the activity, selectivity and stability of the iron catalysts are based upon the commercial operations at Sasol [22].

For operation in the liquid phase, lower temperatures are utilized. Under these conditions CO_2, at least in the presence of significant CO partial pressures, is nearly an inert gas. Thus, the reverse WGS does not occur to a significant extent. This is a major difference between the high and low temperature operations and the impacts of this factor are just being recognized widely.

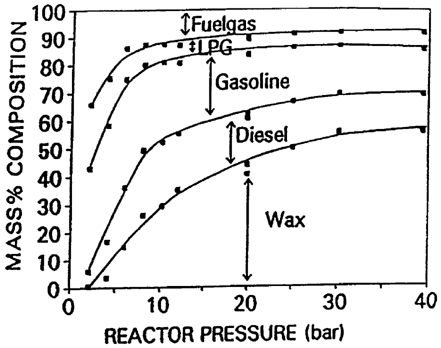

Fig. 7. Mass percentage product distribution as function of reactor pressure at constant superficial velocity for the cobalt catalyst (from Ref. [23]).

9. Pressure

The impact of pressure, at least in the 5–30 atm range, is not very significant, as shown in Fig. 7 [23]. However, our data indicate that operation for long periods at higher pressures (≥30 atm) may cause significantly more rapid catalyst deactivation rate than at lower pressure operations. This activity decline and the shift in product selectivity to lighter products will set upper limits for the pressure used for FTS with iron catalysts.

10. Catalyst phase changes

Operation at lower temperatures provides catalyst phase changes that may differ from those observed at higher temperature operations [22]. We have withdrawn, at increasing intervals of time-on-stream, samples from a CSTR that is operated at low temperature conditions. The phase present following activation in CO is essentially that of iron carbide (90% or greater). Phase changes occur during catalyst usage and these depend upon the catalyst composition. With an unpromoted iron catalyst, both the decline in catalytic activity and the transformation of the carbide phase to Fe_3O_4 occur rapidly (within 200 h) and at about the same rate [24,25]. On the other hand, the same catalyst except that it contains about 1.5 K/100 Fe retains the carbide phase but declines in activity at about the same rate as the unpromoted iron catalyst. The addition of silica is shown to impact the retention of the carbide phase, an unexpected result. The presence of both K and Si cause synergistic effects for both the activity and carbide phase stability. Catalytic activity declines slowly, at less than 1% CO conversion/week, and the carbide phase declines to about 50% of the iron phases and then remains constant during about 3000 h of synthesis. Thus, the catalyst undergoes phase transformations that are dependent upon catalyst composition [24,25]. Studies are underway to relate the changes of a specific catalyst to process conditions.

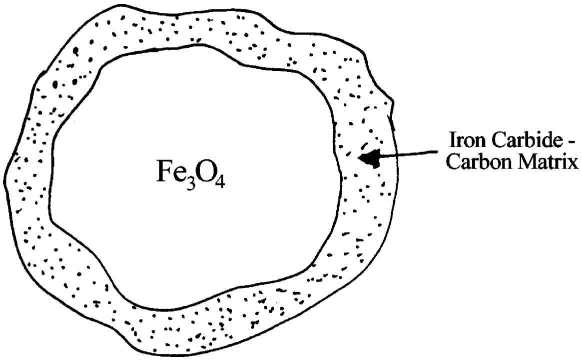

Fig. 9. Schematic of the phases present in a stable iron catalyst during synthesis.

The difference between a catalyst with significant carbide phase and a material that is essentially the Fe_3O_4 phase is illustrated by the data in Fig. 8 [26]. A low alpha iron catalyst that did not contain copper was activated with synthesis gas and exhibited low (20%) CO conversion during about 100 h of synthesis. Samples of this catalyst withdrawn during the 100 h low CO conversion synthesis period were essentially the Fe_3O_4 phase. After this period the hydrogen flow was terminated and the catalyst was exposed to CO for 24 h. Following the treatment with CO, the material contained about 35% carbide phase, the remainder being Fe_3O_4. The CO conversion after the CO activation, following a short induction period, was greater than 90%. The same catalyst material, when initially

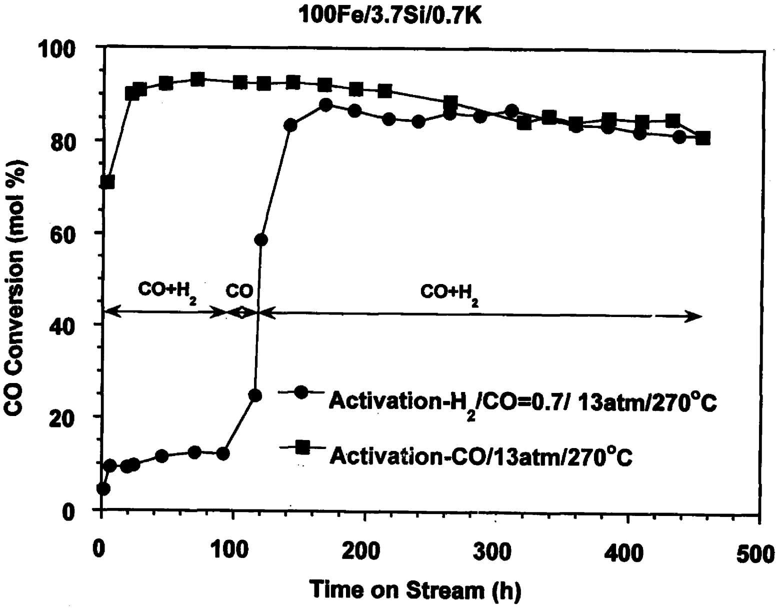

Fig. 8. CO conversion for portions of the same catalyst activated in CO (■) and in syngas ($H_2/CO = 0.71$) followed by activation in CO following about 100 h of synthesis (●).

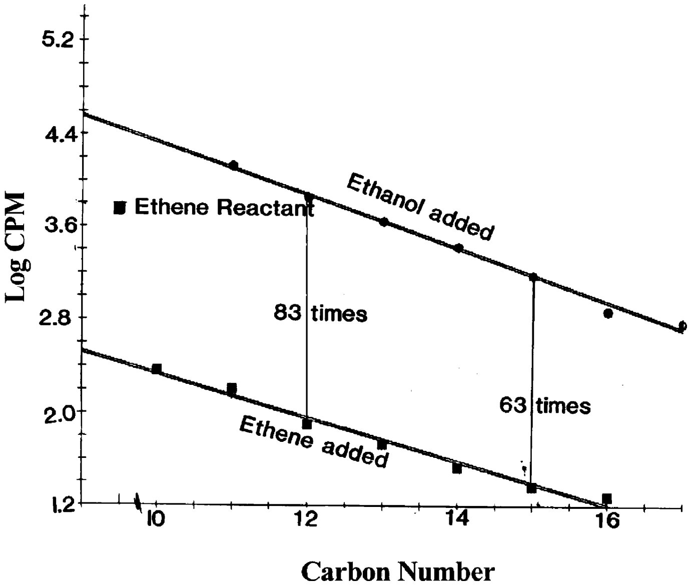

Fig. 10. Radioactivity in hydrocarbons produced during synthesis using a low alpha iron catalyst (UCI C-73) during the addition of ^{14}C-labeled ethanol (●) or ^{14}C-labeled ethene (■).

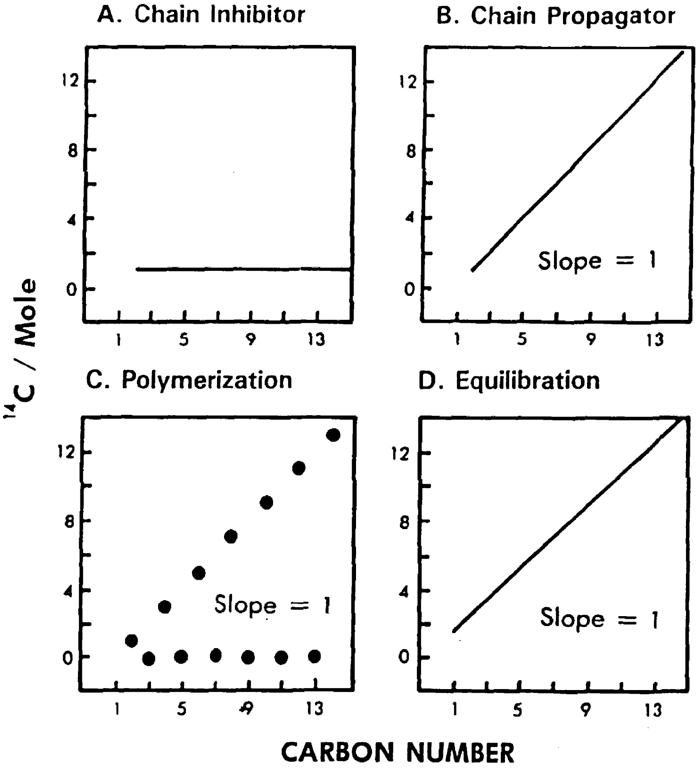

Fig. 11. Schematic representation of ^{14}C activity by carbon number for four chain growth mechanisms.

pretreated with CO, exhibited a CO conversion that was greater than 90% and was very stable, the activity declining at a rate of less than 1% CO conversion/week. Thus, the activity of the carbide phase is at least five times greater than that of the material which is the Fe_3O_4 phase. Based on this and much additional data, a model was proposed for an iron catalyst that contains both potassium and silica promoters that consists of a core that is essentially Fe_3O_4 and a surface layer of iron carbide that surrounds the Fe_3O_4 core (Fig. 9).

11. Reactor

Fixed or fluidized bed and liquid phase reactors have been utilized at the commercial scale for FTS. The reactor used has the potential to impact activity and selectivity, many times in a form that is disguised. The magnitude of these factors is far beyond the scope of this overview [1]. One aspect of the disguises is illustrated in the following section.

12. Isotopic tracers

We have utilized both stable (deuterium) and radioactive (^{14}C) to study the reaction mechanism. The addition of deuterium labeled alkanes has produced data to definitively show that alkanes are completely inert under the reaction conditions, including H/D exchange reactions. Alkenes do undergo exchange but the rate of exchange in the vinyl positions is much more rapid than in other positions [27].

The use of ^{14}C-labeled alcohols and alkenes have demonstrated that alcohols undergo chain initiation reactions with an iron catalyst at a rate that is 50–100 times greater than the alkene of the same carbon number (Fig. 10) [28]. While alkenes do incorporate using a cobalt catalyst, alcohols are nearly inert with this catalyst. Thus, it appears that the fundamental initiation and possibly the chain growth portions of the synthesis are different for cobalt and iron catalysts. The following material applies only to the iron catalyst.

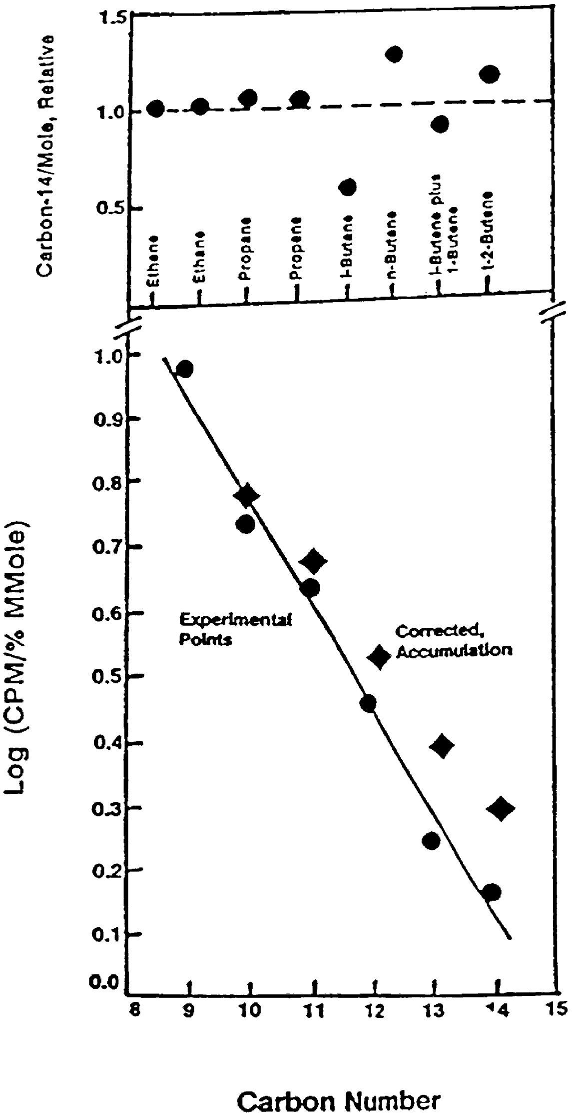

Fig. 12. ^{14}C in C_2–C_4 products (top) and C_9–C_{14} (bottom) products during synthesis with an UCI C-73 iron catalyst and the addition of ^{14}C-labeled ethanol.

Chain initiation by a ^{14}C-labeled alkene or alcohol would produce products that have a constant ^{14}C per mole with increasing carbon number product (Fig. 11) [28]. All other reasonable schemes of incorporation of the ^{14}C-labeled compound added to the synthesis gas leads to an increase in the ^{14}C per mole with increasing carbon number products. The initial results we obtained for the addition of ^{14}C-labeled alcohols were puzzling. For the low carbon number products (C_2–C_4) the added ethanol served to initiate chain

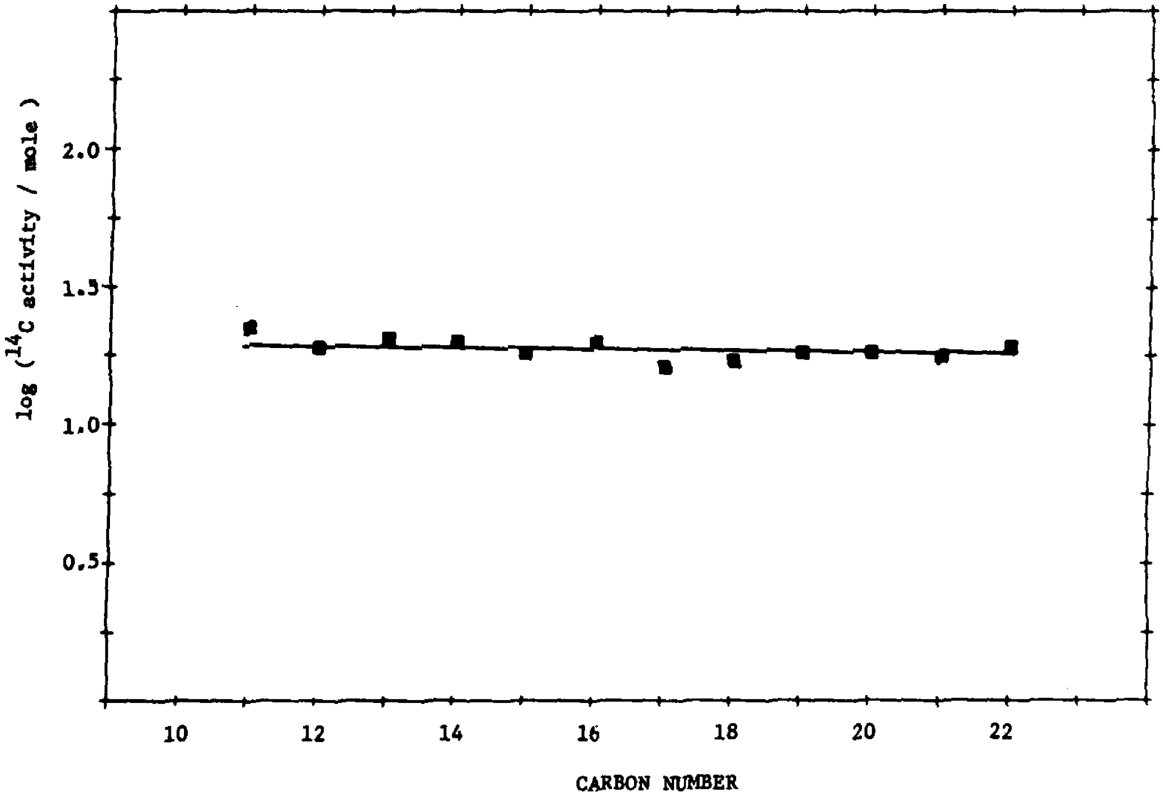

Fig. 13. Radioactivity in products formed during addition of ^{14}C-labeled ethanol to synthesis gas at 1 atm pressure.

growth (top, Fig. 12) [28] and this agreed with earlier results reported by Emmett and coworkers. However, the ^{14}C per mole decreased with increasing carbon number for the higher products (bottom, Fig. 12) [28]. We interpreted these early results to support synthesis using two sets of active sites. One set of sites produced the lower alpha value products and was initiated by the added alcohol. The second set of sites formed the higher alpha products that were only paraffinic and was not initiated by the added alcohol. Thus, the paraffins formed on the sites that produce the higher alpha products simply diluted the ^{14}C-labeled products produced by the low alpha chain growth, resulting in a decrease in ^{14}C per mole for higher carbon number products as shown in the bottom of figure (Fig. 12) [28].

Additional studies have shown that the above ^{14}C-labeled alcohol results are impacted by reactor disguise. When the reaction was run under the same conditions except at atmospheric pressure using a

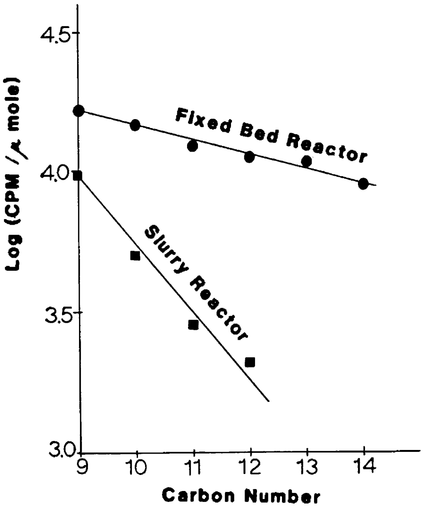

Fig. 14. Comparison of the activity in the alkene fraction from the Fischer-Tropsch synthesis when ^{14}C-labeled 1-pentanol was added to a fixed-bed or CSTR (7 atm, 260 °C).

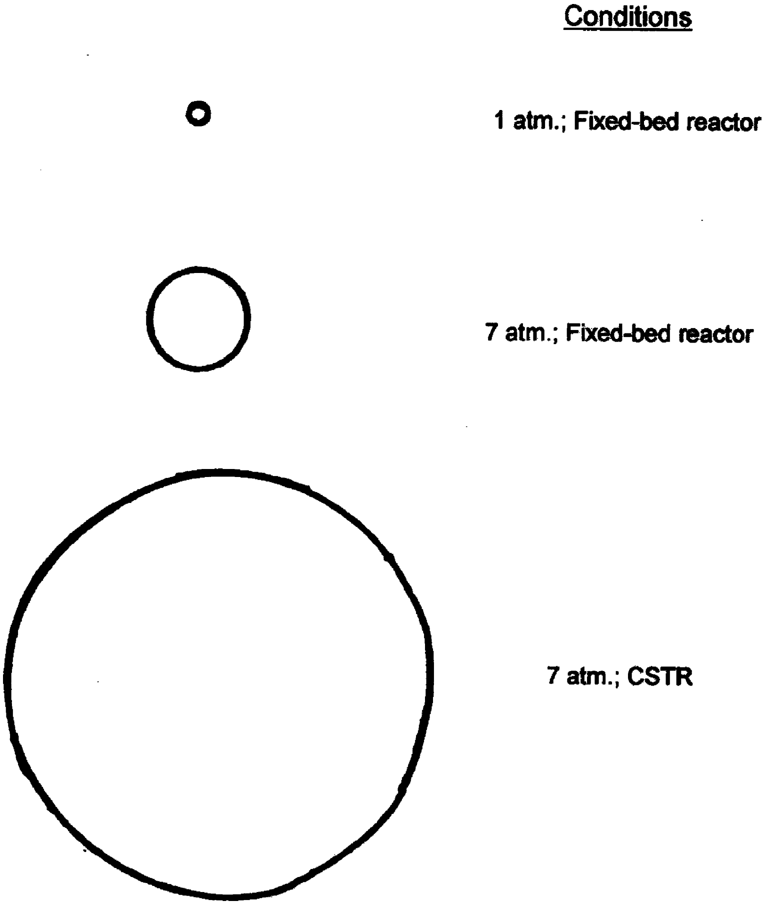

Fig. 15. Schematic of accumulated liquid in various reactors.

fixed-bed reactor, the results were as expected and in agreement with those obtained by earlier workers (Fig. 13) [29]. However, the results obtained in a fixed-bed reactor at 7 atm pressure (0.071 Mpa) the ^{14}C per mole decreased with increasing carbon number but not to the extent that it did in the CSTR (Fig. 14) [29]. The explanation is that dilution of the labeled paraffins by unlabeled products, primarily paraffins, that accumulate prior to tracer addition, and not because of two sets of sites that have different reaction pathways, is responsible. Instead the paraffins are accumulated in the reactor during the period of synthesis that preceded the addition of the ^{14}C-labeled alcohol. At atmospheric pressure in the fixed-bed reactor, little liquid products are held up in the catalyst void space. When the pressure in the fixed-bed reactor is increased to 7 atm, the amount of liquid in the same volume of catalyst void space is larger than at atmospheric pressure, and the ^{14}C-labeled decreases with increasing carbon number. In the CSTR, with a reservoir of about 300 cc of hydrocarbons, the products produced from the labeled alcohol that was added are diluted by the large volume of unlabeled product that has been produced prior to the addition of the labeled compound as illustrated by the schematic shown in Fig. 15 where the size of the circles represents the volume of liquid retained in the reactor zone containing catalyst. This has been verified by more recent results. The higher carbon number products produced during synthesis using the CSTR were separated into alkene and alkane fractions using dry silica gel column chromatography. The paraffins that

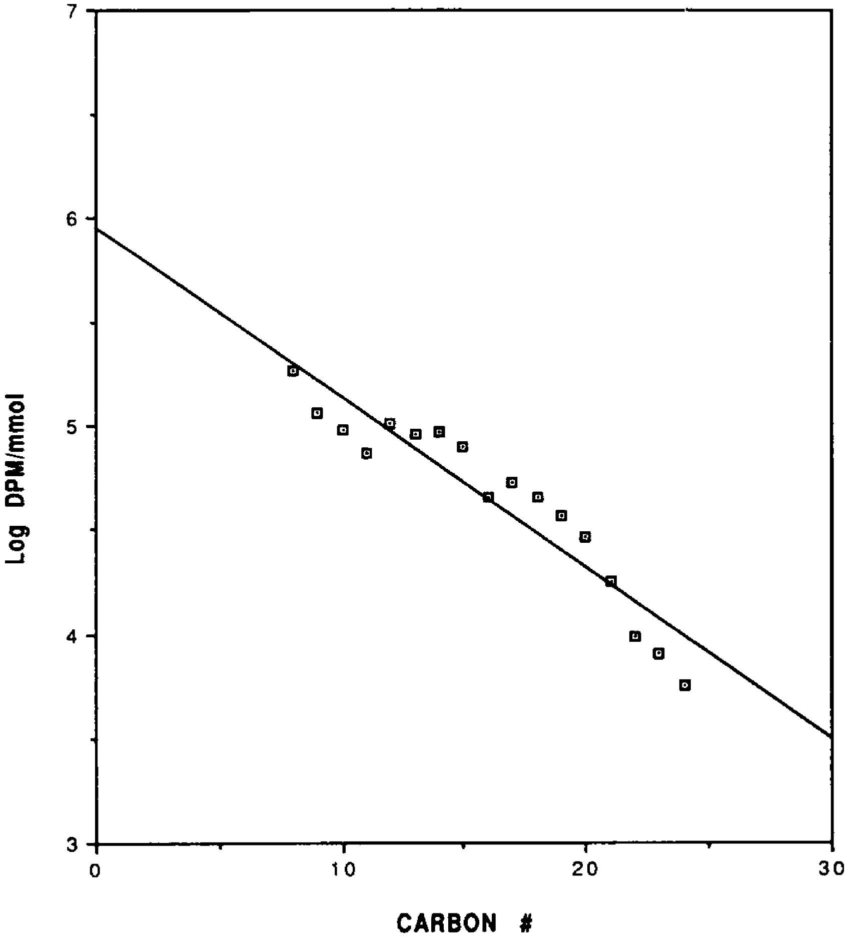

Fig. 16. Plot of log (DPM/mmol) versus carbon number for alkane fraction produced during synthesis with the addition of ^{14}C-labeled ethanol.

were collected exhibited the same trend of decreasing ^{14}C per mole with increasing carbon number as was obtained for the total products obtained from the runs in the CSTR (Fig. 16) [30]. However, the ^{14}C per mole was constant with increasing carbon number for the alkenes (Fig. 17) [30]. The higher carbon number alkenes that are produced during FTS are held in the liquid phase, due to vapor–liquid equilibrium, for longer times than the lower carbon number compounds. The alkenes that are held up in the liquid are hydrogenated to produce paraffins and these accumulate to increasing levels with increasing carbon number. The fraction of alkene/alkane for each carbon number is not constant with respect to the accumulated products; this fraction decreases with increasing carbon number to approach zero. Thus, dilution of the labeled alkenes by accumulated alkenes is negligible. On the other hand, the dilution of the alkanes that are produced during the addition of the ^{14}C-labeled compound by alkanes that are accumulated increases with increasing carbon number. For mechanistic considerations, it is the ^{14}C per mole of the alkenes that should be used. On this basis, the results for the lower and the higher carbon number compounds are in agreement with the added alcohol serving to only initiate chain growth and is consistent with the products being formed by a single alpha mechanism.

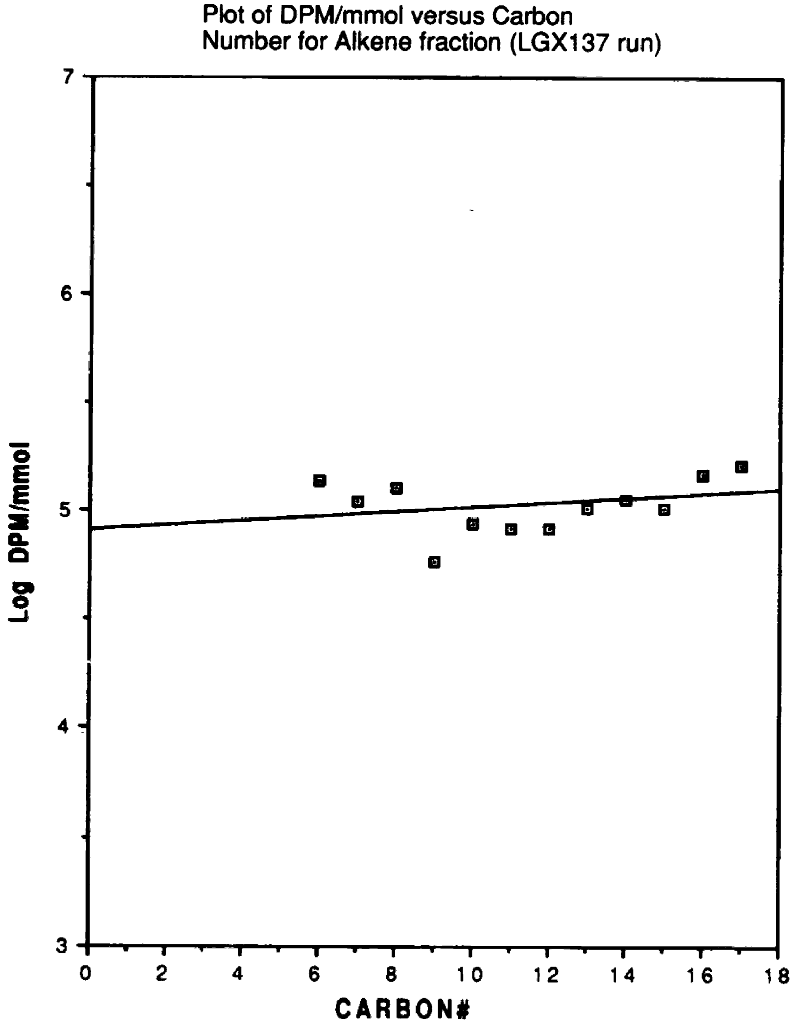

Fig. 17. Plot of log (DPM/mmol) versus carbon number for alkene fraction produced during synthesis with the addition of ^{14}C-labeled ethanol.

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