Summary

The kinetic isotope method (KIM) has been utilized in a study designed to determine the way in which promoters for iron catalysts impact the variety of primary and secondary reactions in the Fischer-Tropsch synthesis (FTS). The KIM involves the addition of known or suspected intermediates to the synthesis gas feed. In order to follow the conversion of the added compound, and the products formed as a result of the addition, the added compound is labeled with a radioactive isotope of carbon. An analysis of the Fischer-Tropsch synthesis products readily permits one to identify those compounds that are derived from the added compound. Using this technique, results were obtained with unpromoted iron, iron promoted by nonreducible oxide, and alkali promoted iron catalysts. A number of anticipated results were obtained as well as some demanding experimental difficulties that were not anticipated from the published results summarized in the Introduction of this report.

A combination of gas chromatographic, dry column chromatographic and liquid chromatographic techniques allowed us to determine the ^{14}C present in compounds over the C_1 - C_{22} range in the alkane and alkene fractions. This permits a more detailed examination of the Fischer-Tropsch synthesis than has been the case with most of the earlier work.

A continuous stirred tank reactor (CSTR) was used for most of the experimental studies. There are many advantages to this reactor system, including constant temperature and exposure of the entire catalyst fill to the same reaction environment. However, it was observed that holdup of heavier products in the CSTR, combined with the slow rate of production of these heavier products, causes severe problems in conducting the ^{14}C tracer studies. These problems are not unique to the KIM technique but are equally important, but largely ignored to date, for non-isotopic process studies where temperature, pressure, etc. are varied and mass balance is used to judge the impact of these process variables. Tracer techniques provide a preferred method to generate experimental data to quantitatively account for the impact of accumulation in process studies utilizing a CSTR.

Severe accumulation problems were encountered even for as low boiling components as ethanol. Several hours were required for the accumulation factor to be eliminated when ethanol was added to the CSTR. The time required to attain "steady-state" becomes progressively longer as the molecular weight, and hence the boiling point, is increased. The unanticipated accumulation of unlabeled compounds, especially C_{10}^+, in the CSTR caused the ^{14}C labeled products, formed during a period of addition of a labeled compound to the syngas feed, to be diluted with unlabeled compounds that were formed and accumulated during earlier periods of operation with unlabeled synthesis gas. Thus, a major fraction of the C_{20} alkane, for example, collected during the 24 hour period of ^{14}C labeled compound addition was formed during a prior period of operation with unlabeled synthesis gas. The magnitude of this problem only became apparent as this experimental program progressed.

Even with the problems encountered with the accumulation factor, it was demonstrated that the added alcohol or alkene served primarily to initiate growing chains. It was shown that the type and extent of secondary reactions that the added compound undergoes depends upon molecular weight and compound class.

It was observed that added pentene did not undergo either isomerization to other pentenes nor hydrogenation to pentane. This is an important observation that could only be made with ^{14}C labeled intermediates. The fact that 1-pentene did not undergo measurable reaction eliminates Fischer-Tropsch synthesis mechanisms that involve liquid or gaseous alkenes as intermediates from consideration as significant reaction pathways for the Fischer-Tropsch synthesis. In other words, C_5 Fischer-Tropsch synthesis products are formed form the chain growing on the surface, or from non-alkene intermediates, and the amount of chains producing C_5 products initiated by liquid or gaseous alkene intermediate compounds is insignificant. This implies that the Fischer-Tropsch synthesis primary product selectivity is essentially determined by the surface reaction, and is only altered by secondary reactions that are a result of reactor and/or process conditions.

Ethene was observed to be a unique alkene. The extent of hydrogenation was much greater than for pentene; based on reported alkene hydrogenation studies this was expected. Ethene also served to initiate chain growth but to a smaller extent than 1-decene. Unlike either pentene or decene, ethene also incorporated into growing chains as well as serving to initiate these chains; this was indicated by the increase in ^{14}C/mole in the hydrocarbon products in C_{16} - C_{22} range.

1-Decene was held up in the reactor so that it underwent significant conversion (10% hydrogenation and 10% incorporation to produce higher carbon number compounds). Thus, accumulation is the major factor in observing alkanes rather than alkenes as the "primary" products in the C_{15} range.

Alcohols undergo more extensive incorporation than the corresponding carbon number alkene does; however, this difference decreases as the carbon number increases. Alcohols and the corresponding aldehyde or ketone are at or near their equilibrium composition under our experimental conditions. Surprisingly, alcohols are hydrogenated to form the same carbon number alkane at a faster rate than it is dehydrated to the alkene; consequently, alkenes are not formed in the Fischer-Tropsch synthesis by dehydration of alcohols that have desorbed to become a part of the liquid or gas phase.

It was observed that similar hydrocarbon product selectivities are obtained at both 1 and 7 atmosphere conditions. Thus, a plot of the percent alkane in the hydrocarbon products has a high percentage of ethane, there is a rapid decline in alkane percentage to a minimum of about 20% for the C_4 - C_5 carbon number products, then a gradual increase in the percent alkane is observed with increasing carbon number until at about C_{15} - C_{20} an alkane percentage of *ca*. 80% is attained, and for carbon numbers greater than *ca*. C_{20} the percent alkane remains constant. It was observed that alkali promoted and unpromoted iron catalysts showed the same shape curve for a plot of percent alkane versus carbon number; however, the alkali promoted catalyst consistently produced hydrocarbon products with about 10% less alkanes throughout the carbon number range C_2 to C_{20}. The surprising result was that alcohol, added to the syngas feed, had the same impact upon an unpromoted iron catalyst as promoting the catalyst with alkali did. Thus, both alkali and added alcohol have the same effect upon alkane selectivity. It is not established yet whether this is due to the alcohol acting as a promoter analogous to alkali or to inhibition by a competitive adsorption. The effect of alcohol occurs only with the unpromoted iron catalyst; no change in the percentage of alkanes was noted when alcohol was added to the syngas feed to an alkali promoted catalyst. The effect of alcohol upon the unpromoted iron catalyst was reversible; the alkane selectivity gradually (ca. 24 hours) returned to the pre-alcohol period upon termination of the alcohol addition. This effect prevents us from obtaining a product distribution for alcohol incorporation for an unpromoted iron catalyst.

The patterns of ^{14}C distribution in the products for alcohols and for alkene incorporation were similar; the major difference was the extent of incorporation. This was true for both the alkali promoted and the alkali free catalyst.

A comparison of the ^{14}C activity in the C_4 products from the conversion of ^{14}C labeled 1- and 2-propanol was revealing. The 1-propanol produced predominately normal alkenes and alkanes while the 2-propanol (isopropyl alcohol) produced predominately isoalkenes and isoalkanes. Thus, these two alcohols form surface intermediates that initiate chain growth but do not interconvert to become equivalent. Furthermore, the relative amount of chain initiation indicates that 1-propanol is ca. 10 times more effective than 2-propanol; this is near the ratio that normal and iso hydrocarbons are produced during normal Fischer-Tropsch synthesis with an iron catalyst.

Ethene provides evidence for carbonylation:

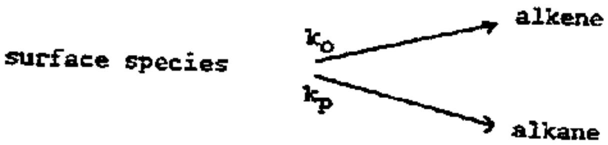
$$CH_2 = CH_2 + CO,\ H_2 \longrightarrow CH_3CH_2CH_2OH.$$

However, carbonylation represents a minor fraction of the total ethene conversion. With the pentenes and 1-decene, carbonylation was such a small fraction of the total conversion that it could not be detected.

The use of ^{14}C labeled alkenes has permitted us to answer the question concerning alkene incorporation and the extent of their incorporation. Chemical analysis alone was unable to make this quantitative determination.

For promoters it was shown that some of the non-reducible oxides may provide a second catalytic function, especially for the secondary reactions of oxygenate products. Sodium, an alkali promoter, and added alcohol produce similar effects, they decrease the amount of secondary hydrogenation to alkanes. It appears, based upon data obtained by the addition of C_2, C_5 and C_{10} ^{14}C labeled alkenes, that alkanes comprise ca. 20% of the primary products for each carbon number fraction in the C_2 to C_{22} range. The products observed attain this value only for the C_4 - C_5 fractions. Higher alkane percentages for the C_2 and C_3 fractions are a result of the rapid hydrogenation of the primary alkene products; this was verified by the data produced when ^{14}C labeled ethene was added to the syngas. Secondary hydrogenation reactions did not occur with added ^{14}C labeled 1- or 2-pentene; hence, the observed alkane/alkene distribution represents the primary product distribution. For higher carbon number products, accumulation in the reactor increases the residence time for secondary reactions. Thus, the hydrogenation of C_{10} alkenes is much slower than for ethene; however, accumulation and the longer reaction times allow for a significant contribution by secondary hydrogenation reactions to produce alkanes. The

1-decene data support this latter statement. Thus, the alkali promoter may alter the ratio k_o/k_p shown below



to favor alkene products. However, it appears that the added alkene altered the ^{14}C incorporation pattern.

I. INTRODUCTION

I-A. Promoters

The Fischer-Tropsch synthesis received enormous attention since it was first announced (I-1). In 1951 Storch et al. (I-2) summarized much of the early work. Anderson (I-3, I-4), among others, has continued to review much of the work, especially that directed toward an understanding of the mechanisms of the catalysis involved in the reactions.

Early work utilized a cobalt catalyst (I-1). A combination of factors, but mainly supply and cost, caused commercial operations to switch to iron based catalysts. An iron catalyst could only be utilized for an extended period if it was promoted. Thousands of catalyst formulations have been tested; Emmett alone characterized by both physical and chemical adsorption measurements more than 1,000 iron based catalysts, and tested these for ammonia synthesis activity. Thus, the commercial interest in Fischer-Tropsch and ammonia synthesis has been responsible for extensive studies that led to an enormous body of information on promoted iron catalysts.

Promotion of heterogeneous catalysts is probably the most widely practiced and least understood aspect of modern catalysis. More than 70 years ago in his book on catalysis Jobling has a section on promotion; he says, "It has recently been discovered that there are other substances which, when added in minute quantity to a catalyst, increase its activity. Thus practically all metallic catalysts become activated when certain oxides or compounds or other metals are distributed throughout them. In Haber's synthetic ammonia manufacture, for instance, the iron, platinum, osmium or uranium employed as a catalyst is quickened to an enormous extent by the presence of traces of salts of other metals or, with certain exceptions, of the other metals themselves. Further research in connection with these promoters, as they are called, would be amply repaid."

Promotion in heterogeneous catalysis was recently reviewed by Thomson (I-6):

"This lecture reflects the variety of promotional effects. The examples have been taken mainly from the 1985-86 literature. The word promotion does not occur frequently in the titles of papers on catalysis. Yet the majority involve promotion or modification of solids. The survey could only be made by reading papers regardless of their titles. It was obvious that the emphasis for promotion had shifted from acceleration to specificity, selectivity and lifetime of catalysts."

In general, two types of promoters are added to iron catalysts: one is an alkali promoter, almost always a Group I and/or II element, and the other is a structural promoter, a non-reducible metal oxide, added to prevent a rapid loss of surface area. The variety of test conditions for catalyst characterization and activity testing make it a very demanding task to compare results from the various studies. This difficulty is illustrated by the following two examples.

Alkali metals have been utilized extensively as a promoter for iron catalysts, and in many cases more than one of these metal oxides are added. Even so, a precise role for the alkali metal has not been adequately defined. This has been described recently by Dry (I-7); he emphasized that the influence of promoters upon activity may depend upon reaction conditions. An illustration of this is shown in figure I-1. Here it is seen that in one case the relative activity increases as the alkali content of the catalyst increases; in the other case just the opposite trend is observed so that alkali appears to function as a poison.

The alkali also does not impact all reactions in the same manner; hence, the selectivity may be altered by the addition of promoter. As indicated by Professor Thomson, this is viewed as an area for emphasis in today's studies. In the Fischer-Tropsch synthesis it is frequently observed that the product distribution does not follow a simple Anderson-Schulz-Flory distribution (I-3); rather a plot is obtained which appears to require two independent polymerization pathways to describe the products in the C_1-C_{20} range. This phenomena, the need for two alpha values (slope of the straight line in the Anderson-Schulz-Flory plot) is illustrated in figure I-2. These plots with two alphas were obtained in larger pilot or commercial plants using fixed or fluidized catalyst beds as well as in smaller laboratory reactors. Thus, their existence should not be questioned. Some workers, e.g. Schliebs and Gaube (I-8) attributes this two alpha phenomenon to the presence or absence of alkali promoters. As shown in figure I-3, the unpromoted iron catalyst exhibits just one linear plot whereas the potassium containing catalyst exhibits two lines with a break at about carbon number 10. The slope, the ratio of polymer growth to product formation plus polymer growth, corresponding to the lower carbon number compounds is the same for both catalysts. The higher alpha value, if it is due to sites formed from alkali promotion, means that the alkali induced sites cause polymerization by chains which grow to a much higher average carbon number than those grown on the unpromoted sites.

In addition to the selectivity changes due to the two, or more, alpha values, there appears to be a general consensus that alkali causes the catalyst to have a lower hydrogenation activity so that the hydrocarbons produced by these catalysts have a more olefinic character.

For a more detailed discussion of promoter action one should consult recent reviews, e.g. I-4.

I-B. Isotopic Tracer Studies

I-B-1. Emmett and Coworkers

Fischer and Tropsch (I-9) suggested that the metallic carbide was the intermediate in the synthesis of hydrocarbons from carbon monoxide and hydrogen over the catalysts iron, nickel and cobalt catalysts. This theory was widely accepted following its introduction. The availability of a radioactive carbon isotope, ^{14}C, provided a means of testing this theory (I-10). The general plan of these experiments was quite simple. If the carbide was an intermediate, a surface layer of metal carbide containing radioactive ^{14}C should cause the initial hydrocarbon products formed by exposing a mixture of hydrogen and normal carbon monoxide (^{12}CO) to the

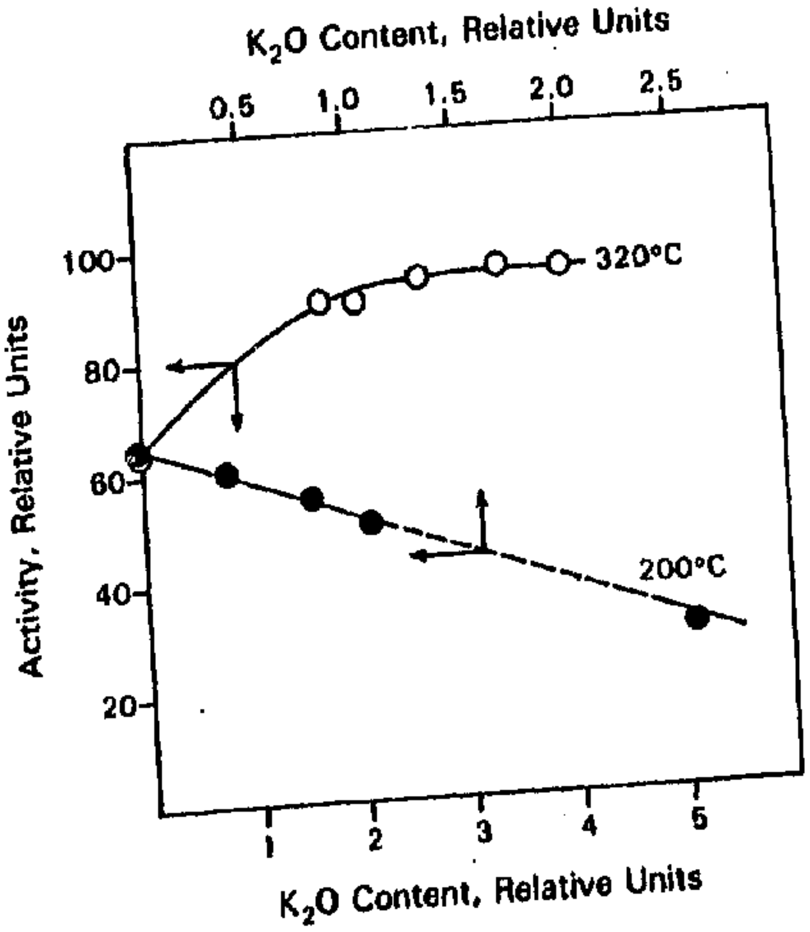


Figure I-1. Dependence of activity change for an iron catalyst with the amount of alkali promoter (data from reference I-7).

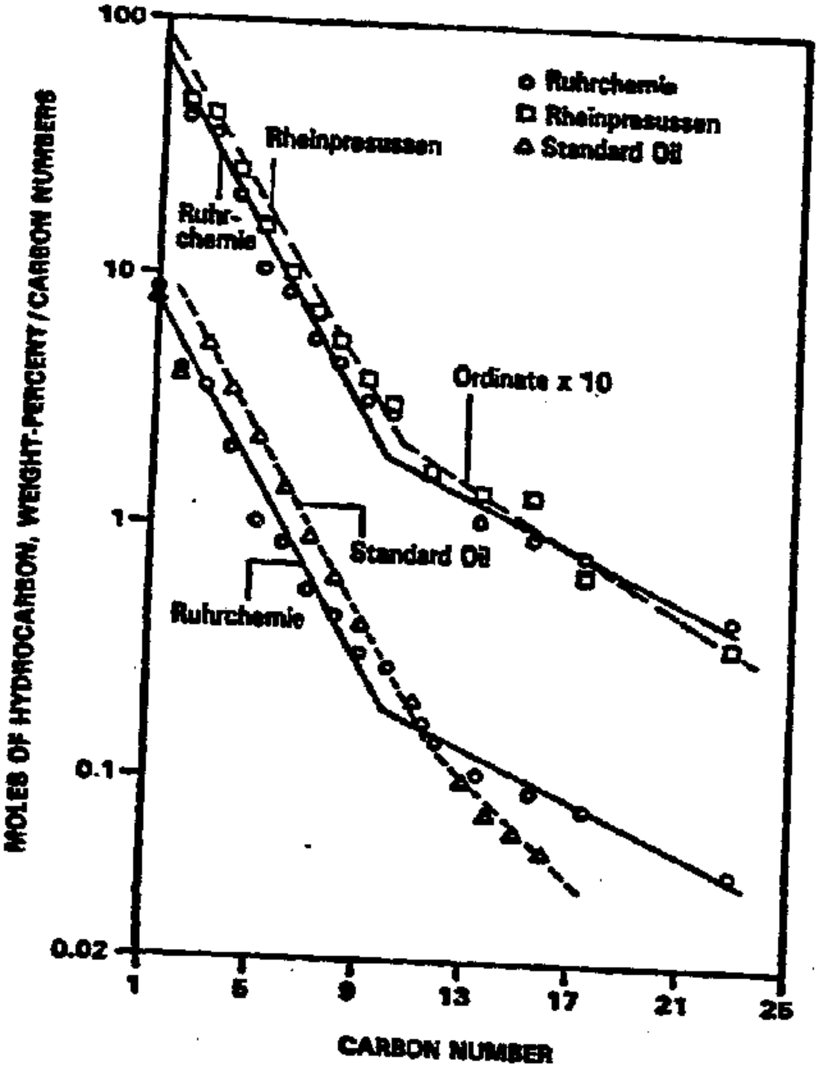


Figure I-2. Logarithmic plots of moles against carbon number. Hydrocarbons Schwarsheide tests compared with those from fluidized synthesis (from reference I-3).

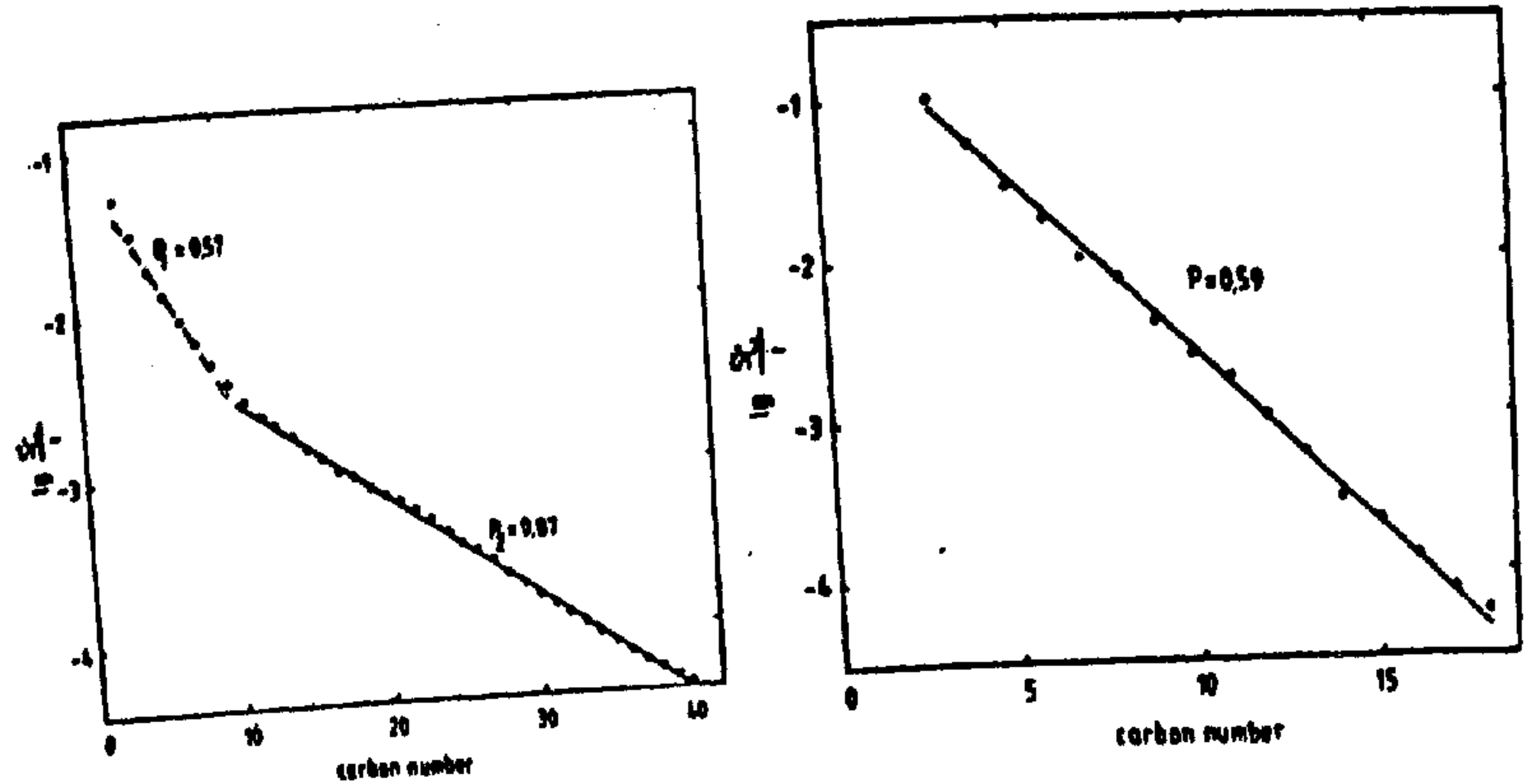


Figure I-3. Mole fraction of hydrocarbons (normalized to C_3-C_{40}) versus carbon number iron catalyst without K_2CO_3 (right figure); iron catalyst with $m_{K_2CO_3}/m_{Fe} = 0.02$ (left figure) (from reference I-8).

radioactive carbide at synthesis conditions to be approximately as radioactive as the surface. Similarly, a surface carbided with non-radioactive carbon monoxide should, on contact with a H_2-^{14}CO mixture, at first form hydrocarbons with much lower radioactivity than that of the H_2-^{14}CO mixture.

Kummer et al. (I-10) prepared the necessary carbided catalysts; most of the studies were conducted with a promoted, fused, synthetic ammonia catalyst containing 2.26% Al_2O_3, 0.62% SiO_2, and 0.21% ZrO_2 as promoters. CO chemisorption indicated that 35% of the catalyst surface was iron, and 65% was promoter. Synthesis was effected at temperatures from 240 to 300°C, ca. 1 atm pressure and, in most cases, $CO/H_2 = 1/1$. Calculations for the fraction of the reaction going by way of iron carbide as an intermediate are shown in figure I-4 as a function of the ratio between the amount of carbon in the synthesized hydrocarbons and the amount that would be required to form a monolayer on the iron surface of the catalyst (assuming the surface carbon to be present in a ratio of one carbon atom for each two surface iron atoms). As can be seen from figure I-4, the data clearly indicate that at temperatures of about 260°C or less, an average of about 10% of the synthesized hydrocarbon appears to have been formed by carbide reduction, regardless of the pressure of synthesis gas, the percent Fe_2C present or the ratio of hydrogen to carbon monoxide in the synthesis gas. They concluded that the mechanism of hydrocarbon production by carbide reduction plays only a minor role in the synthesis of hydrocarbons.

Emmett and coworkers (I-10) also considered whether synthesis could occur on a few active sites of the type proposed by Taylor (I-11). They performed two types of experiments. In one group of runs, care was taken to synthesize an amount of hydrocarbon corresponding to only a very small fraction of the surface. If active points covering several percent of the surface were involved, one would expect that when the total amount of hydrocarbon synthesized was made to correspond to a smaller and smaller fraction of the surface carbon, the apparent percent of the reaction going by way of the carbide mechanism would rise. In contrast to this, even the lowest (0.62% of a monolayer) hydrocarbon synthesis the reaction going by way of a carbide was only 10%. Thus, if active points were responsible for most of the synthesis they must correspond to much less than 0.5% of the surface of the catalyst.

A second type of evidence that argued against the possibility of active points causing most of the synthesis was the fact that successive experiments taken without intervening evacuation showed that the apparent percent of the reaction going by way of the carbide is constant. If active points were influencing the results one would have expected successive runs, or successive samples in a single run, to give successively smaller apparent percentages of the reaction proceeding by way of the carbide mechanism. In contrast, a constant percentage was obtained.

Kummer and Emmett (I-12) used ^{14}C to study the chemisorption of CO as a means of determining the extent of the heterogeneity of the surface of iron catalysts. Roginskii and Todes (I-13) suggested that if the surface is heterogeneous, the portion of the adsorbate added first should desorb last since the highest heat of adsorption, and hence the highest activation energy for desorption, is obtained for the initially adsorbed molecules. The catalyst utilized by Kummer and Emmett was the same as used in the carbide

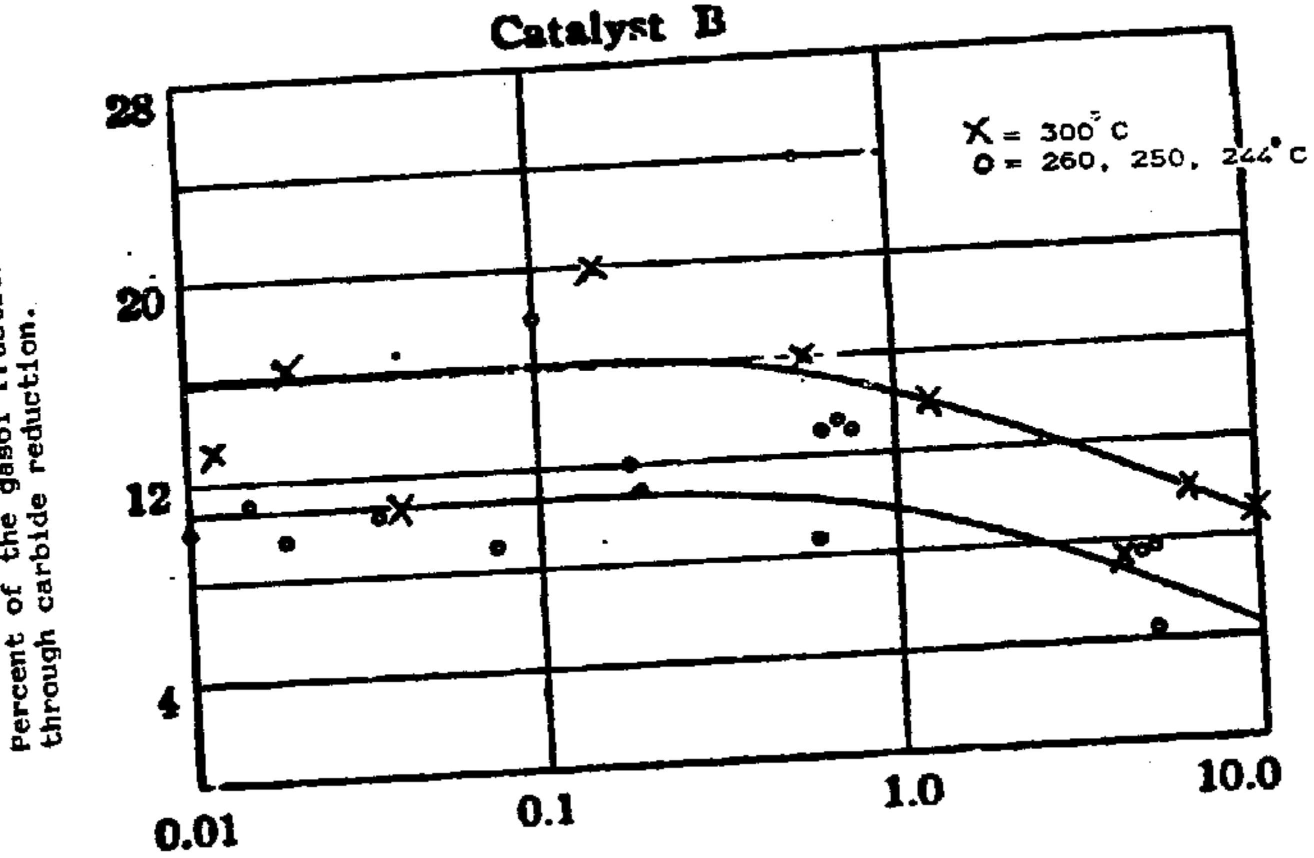


Figure I-4. Hydrocarbons produced as fraction of catalyst surface. (from reference Figure I-4).

studies described above (I-10). The experimental results may be succinctly summarized by saying that about 50% of the surface holds chemisorbed CO in such a way that it can rapidly exchange with any physically adsorbed or gaseous carbon monoxide present and could also rapidly form a homogeneous chemisorbed phase if added in two successive portions. The other 50% of the surface held its chemisorbed CO in such a fashion that it could not exchange rapidly at either -78 or -195°C with physically adsorbed or gaseous carbon monoxide and was therefore distinguishable from other portions of added chemisorbed gas. The simple conclusion is, therefore, that half of the surface behaved as though it were heterogeneous and the other half as though it were heterogeneous. However, Kummer and Emmett pointed out that further considerations indicate that such a clear-cut deduction as to the nature of the catalyst surface was not warranted. They concluded that it was possible to reach the above simple conclusion only if one assumed that on a heterogeneous surface the chemisorbed molecules may occupy fixed positions and do not exchange rapidly with the gas phase, with physically adsorbed CO or with other molecules of chemisorbed carbon monoxide, and that on a homogeneous surface the chemisorbed CO molecules are not sterically hindered from becoming equivalent to each other.

Kummer and Emmett (I-12) also observed that when adsorption was done in two steps there was a very rapid displacement of part of the first fraction of chemisorbed carbon monoxide when one added the second fraction. They offered three possible explanations for this observation:

(1) A fraction of the first portion is desorbed by the high heat of adsorption of the second fraction. This was discounted since the chemisorption of oxygen, with a heat of chemisorption of 122 kcal/mole, did not cause displacement of chemisorbed CO in spite of the fact that oxygen penetrated the CO surface layer to oxidize approximately 10 layers of iron atoms.

(2) A complex, such as $Fe_2(CO)_9$, may form and some of the bridged CO may become equivalent.

(3) The heat of adsorption decreases with surface coverage so that the heat of adsorption decreased to a few kilocalories per mole of CO; this would account for the observed rapid exchange.

Thus, these experimental results were not sufficient to define whether the iron catalyst surface is heterogeneous, or if it is, the extent of heterogeneity.

Kummer et al. (I-14) converted a syngas mixture ($CO/H_2 = 1/1$) that contained either methyl- or methylene-labeled radioactive alcohol over an iron catalyst at about 230°C and 1 atm pressure. Most runs were with a catalyst that contained 2.82% Al_2O_3 and 1.39% ThO_2 promoters. If ethyl alcohol is either an intermediate or if it becomes modified slightly upon adsorption on the catalyst surface to form an intermediate, one would logically expect in the tracer experiment to find a constant molar radioactivity in all hydrocarbon products having three or more carbon atoms. On the other hand, if the alcohol is not an intermediate but is simply degraded to CH_2 groups on the surface or to carbon monoxide, one would expect to find the radioactive carbon distributed as a constant fraction of the carbon atoms in the products.

In preliminary runs with an iron catalyst promoted by 1.55% Al_2O_3 and 0.58% ZrO_2, these authors made a number of observations. First, they noted that the addition of alcohol caused a decrease in the ratio of paraffins to olefins; that is, the added alcohol appeared to inhibit hydrogenation. In a run without added alcohol the ratio of saturated to unsaturated hydrocarbons was 122; in a run with added alcohol this ratio was decreased to 1.1. Secondly, these authors also noted a slight lowering of the overall catalytic activity.

The radioactivity per mole of hydrocarbon was essentially constant for C_2 and higher hydrocarbons (figure I-5). The activity for hydrocarbons greater than C_4 was not determined for individual carbon number hydrocarbons; rather, the number of moles was obtained from pressure-volume measurements for the hydrocarbon and the CO_2 produced by their complete combustion was used to obtain average number of carbons per molecule. A comparison of the molar activity of the hydrocarbons with the activity in the original alcohol indicated that one molecule out of 3 to 4 contained the carbon atoms from the radioactive alcohol. Thus, the results indicated that ethanol, or a C_2 species derived from it, acted as an intermediate in the synthesis of higher hydrocarbons from a CO/H_2 mixture over an iron catalyst.

These authors also degraded the radioactive propane and propylene produced when methyl- or methylene-labeled ethanol was added to the synthesis gas. The propane was cracked at ca. 575°C to produce methane and ethene. Propene was also degraded by converting it first to acetone and then to iodoform. The activity for the methane or iodoform obtained thusly, together with that expected if the carbon from CO added exclusively to the methylene carbon (α addition) are summarized in Table I-1.

Table I-1

Activity Distribution in Propane Formed from ^{14}C Labeled Ethanol During Fischer-Tropsch Synthesis (ref. I-14)

From Propane	CH_4 Activity		CHI_3 from Propene	
Alcohol Added	Observed	Expected	Observed	Expected
$^*CH_3CH_2OH$	880	985	760	985
$CH_3{}^*CH_2OH$	120	0	82	0

Thus, the data are consistent with addition of the CO derived carbon predominately to the α position.

Kummer and Emmett (I-15) obtained data from runs in which primary alcohols (ethanol, n-propanol, or 2-methyl-1-propanol) were added to the extent of about 1.5 volume percent to a 1:1 $H_2:CO$ synthesis gas. Two catalysts were utilized; one contained, before reduction, 2.82% Al_2O_3 and 1.39% ThO_2 in addition to Fe_3O_4 and the other contained 7.95% Al_2O_3 in addition to Fe_3O_4. The synthesis was effected at ca. 235°C and 1 atm pressure. Methanol, 2-propanol, a secondary alcohol, and 2-methyl-2-propanol, a tertiary alcohol, were also utilized. In these runs the gaseous products were

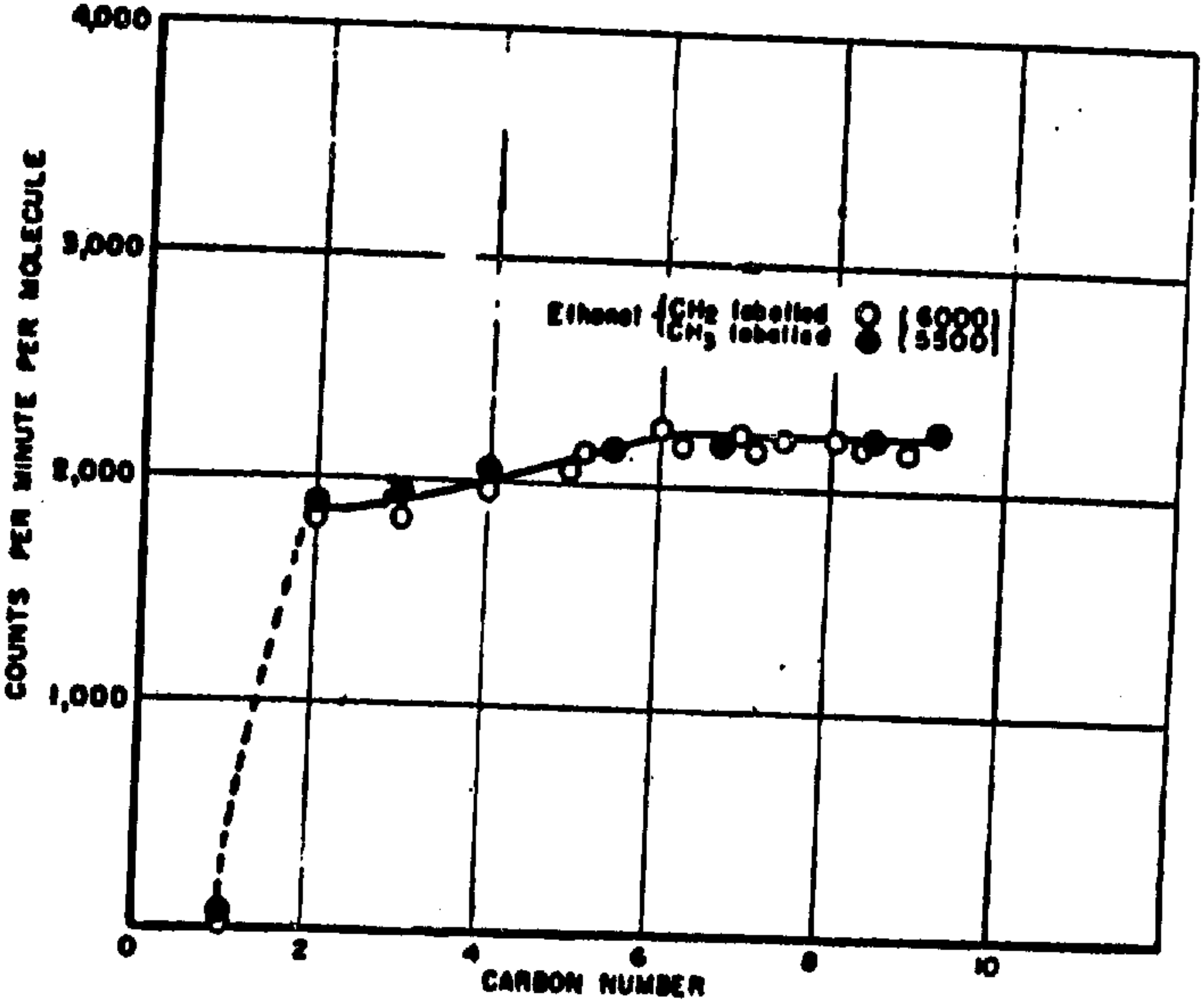


Figure I-5. Activity per cc. of hydrocarbon vapor formed during synthesis runs using an α-labeled (Δ) and a β-labeled (O) ethyl alcohol. The activity of the α-labeled alcohol was 6000 counts per min. per cc. of vapor; that for the β-labeled alcohol was 5500 (from reference I-14).

separated into C_1, C_2, C_3 and C_4 fractions by distillation in a Podbielniak column. In addition, in a few runs 2-methyl propane (isobutane), n-butane, 2-methyl-1-propene (isobutene) and the n-butenes were separated from each other and analyzed for their specific radioactitivies.

The hydrocarbon synthesis products in the C_2-C_{10}, C_3-C_{10} or C_4-C_{10} ranges when ethanol, n-propanol or n-butanol, respectively, were added to the synthesis gas had an approximately constant molar radioactivity equal to one-third to one-half of the molar radioactivity of the original alcohol. Thus, these results indicate that the primary alcohol adsorbed on the iron catalyst to act as an initiator to buildup higher hydrocarbons.

Methanol, when added to the synthesis gas, produced CO_2 that contained much more radioactivity than could have been formed by decomposition to CO followed by water gas shift as depicted below:

$$*CH_3OH \rightleftarrows *CO + 2H_2 \qquad [I\text{-}1]$$

$$*CO + H_2O \rightleftarrows *CO_2 + H_2 \qquad [I\text{-}2]$$

Thus, at least a considerable fraction of the CO_2 was derived by a direct reaction pathway involving radioactive methanol.

When radioactive methanol was added to the syngas, the hydrocarbon activity, when plotted against the carbon number, gave a straight line of a slope of 70 counts/minute/cc of hydrocarbon for each unit increase in carbon number (figure I-6). The amount by which the slope of the line exceeds the activity of the CO (70 versus 32 counts per min. per cc) was taken as evidence that there is a tendency for the complex resulting from adsorbed methanol to enter chain-growth and not just the chain-initiating step. With methanol only about 1 hydrocarbon molecule in 12 appeared to originate from a complex formed by the adsorption of methanol on the catalyst surface. This corresponds to a much lower initiation by methanol than for ethyl, n-propyl or 2-methyl-1-propanol where one in every two or three hydrocarbon molecules were derived from the added alcohol. In addition, methanol, unlike ethyl, n-propyl or n-butyl alcohols, did not alter either the total conversion nor the alkane to alkene ratio from that obtained during control runs with syngas alone made either just before or just after the methanol run. Thus, it appears that the surface species derived from methanol has a behavior that uniquely differs from those derived from higher carbon number normal alcohols.

A comparison of the results obtained when 2-propanol was added to those when 1-propanol was added is most interesting. First, 2-propanol did not enter into the building of higher hydrocarbons to the same extent as the primary alcohols; only 1 molecule in 7 of the C_4 hydrocarbons and 1 in 27 of the C_9 hydrocarbons were produced from the radioactive 2-propanol. Secondly, there was a steady drop in the radioactivity of the hydrocarbon fractions from 900 for the C_4 hydrocarbons to 250 for C_9 hydrocarbons when 2-propanol was added whereas this remained nearly constant when a normal alcohol was added (figure I-7). Thirdly, there was an appreciable difference in the activity of the normal- and branched-butane hydrocarbons; this is illustrated in Table I-2.

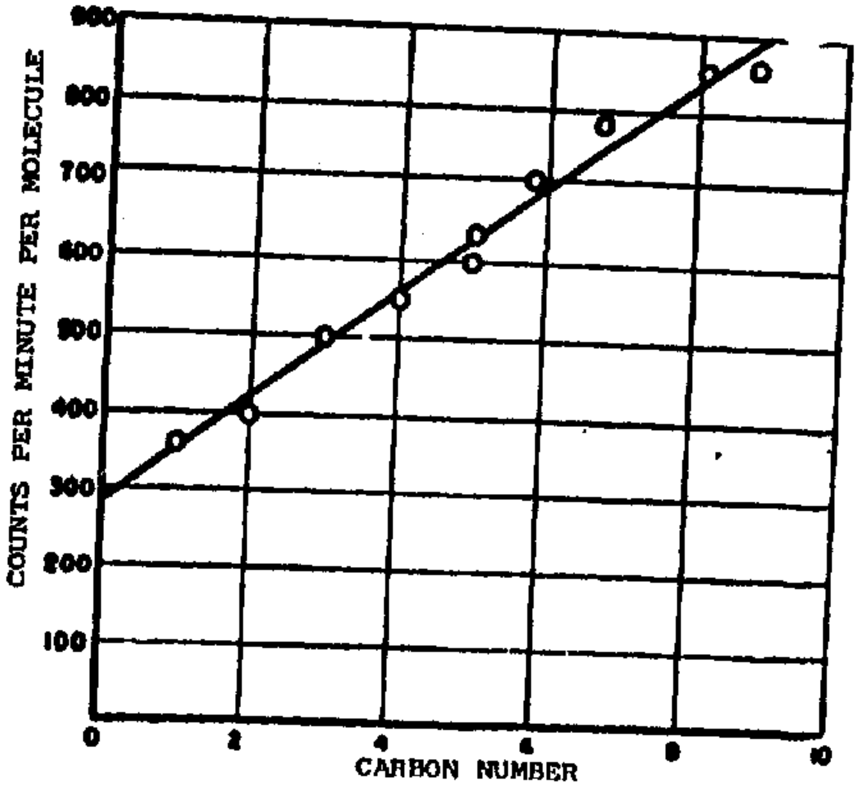


Figure I-6. Radioactivity of products formed when syngas containing ^{14}C labeled methanol was converted with an iron catalyst at one atmosphere (data from reference I-15).

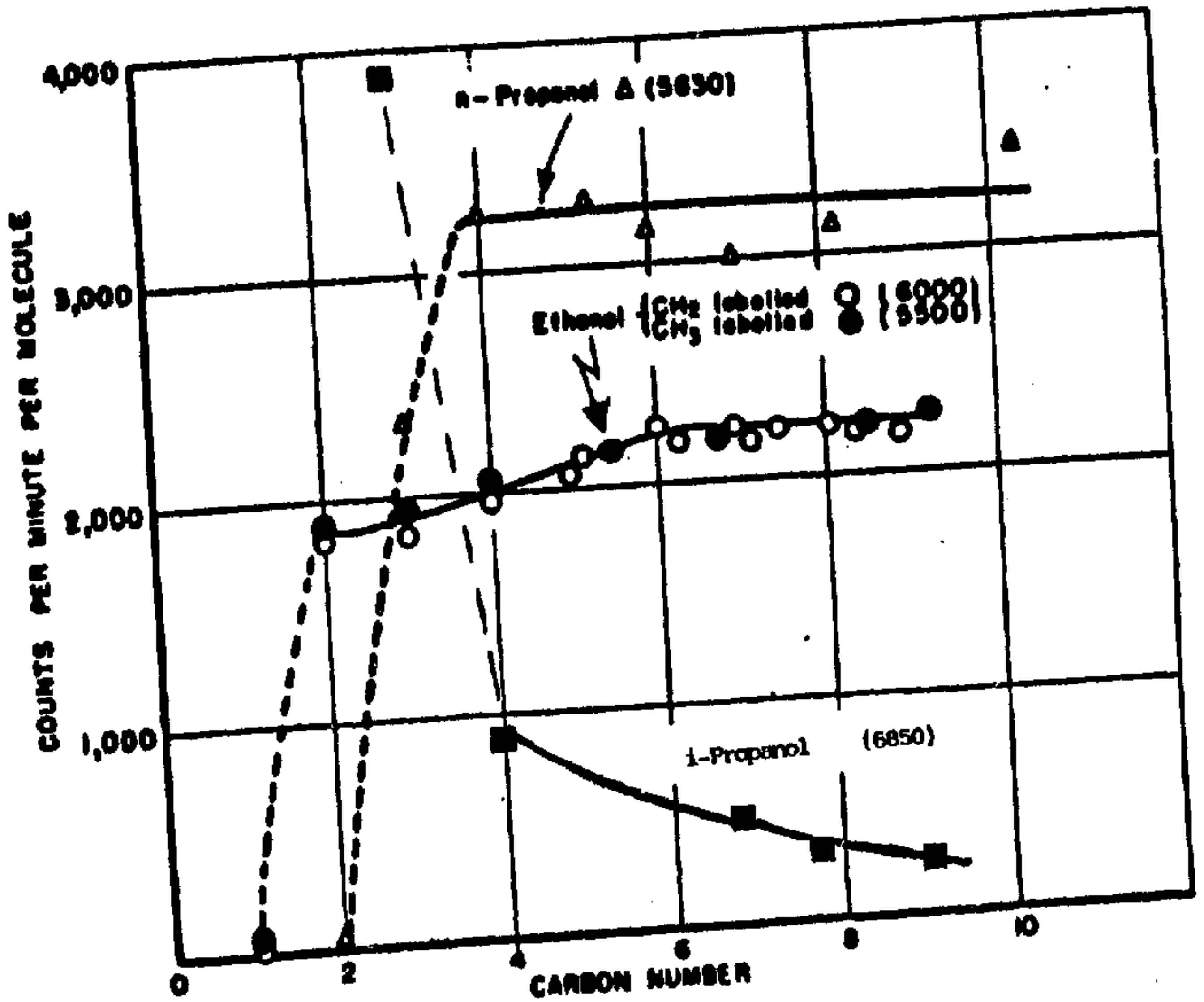


Figure I-7. Same at 1-6 to ^{14}C labeled { then contains ethanol (methyl and methylene labeled), 1-propanol or 2-propanol was converted with a iron catalyst at 1 atom pressure (data from reference I-15).

Table I-2

Activity Distribution in n- and i-butane from the Addition of Labeled Propanols (from ref. I-18)

Alcohol Added	C_4-alkane		C_4-alkene	
	n	iso	n	iso-
$CH_3\ {}^{14}CH_2CH_2OH$	2630	0	2500	450
$CH_3CH_2\ {}^{14}CH_2OH$	3100	0	0	1050
${}^{14}CH_3CHOH{}^{14}CH_3$	30	4370	300±100	4200±30

It is evident that 1-propanol produced n-butane or n-butenes with a high activity but that most, or all, of the i-butane or i-butene was formed directly from the unlabeled CO. The results for the synthesis when 2-propanol was present is just the opposite; the iso-alcohol produces labeled iso-C_4 hydrocarbons but the n-C_4 hydrocarbons are mostly,or exclusively, formed from the unlabeled CO. These above results were clearly presented by Kummer and Emmett (I-15) but in later publications and reviews (even those by Emmett) only the average activity for C_4 hydrocarbons was considered. Thus, this important observation has been ignored for the past 30 years.

Kokas et al. (I-16, I-17) conducted synthesis experiments where labeled ethanol was added to the syngas feed to a doubly promoted iron catalyst (Fe_3O_4 plus 4.6% MgO, 0.6% K_2O, 0.6% SiO_2 and 0.6% Cr_2O_3) with runs at 1, 7.5 and 21 atm pressure. The variation in radioactivity in the products are shown in figure I-8. The qualitative features of the curves obtained at the three pressures are similar. The effect of pressure upon incorporation is clearly evident; the average incorporation falls from 18 to 7 to 2.2% as the pressure increased from 1 to 7.5 to 21 atm. The data obtained at one atmosphere was questionable because of catalyst activity loss with time. Even so, it is clear that the ethanol is acting primarily as a chain initiator. It also appeared that the incorporation of alkali into an iron catalyst decreased ethanol incorporation by a factor of 2.

Kokes et al. (I-16, I-17) also utilized a nitrided iron catalyst which produced a higher fraction of alcohol than the normal iron catalyst did. The activity for hydrocarbon and alcohol products are compared in figure I-9 and it is evident that both compound classes have the same activity. It was therefore concluded that the alcohol and the hydrocarbon product for each carbon number arose from the same surface complex.

These authors also converted syngas containing 1.5 or 0.04% ${}^{14}C$ labeled ethanol using a cobalt catalyst at atmospheric pressure, 190°C and $H_2/CO = 2/1$. The data with cobalt (figure I-10) was similar to that obtained with an iron catalyst except the C_2 products had the highest activity. They attributed this to dehydration of ethanol to form ethene which was then quickly hydrogenated to ethane. This would cause the ethane to contain a high fraction of material derived from ethanol, and hence the higher activity. It

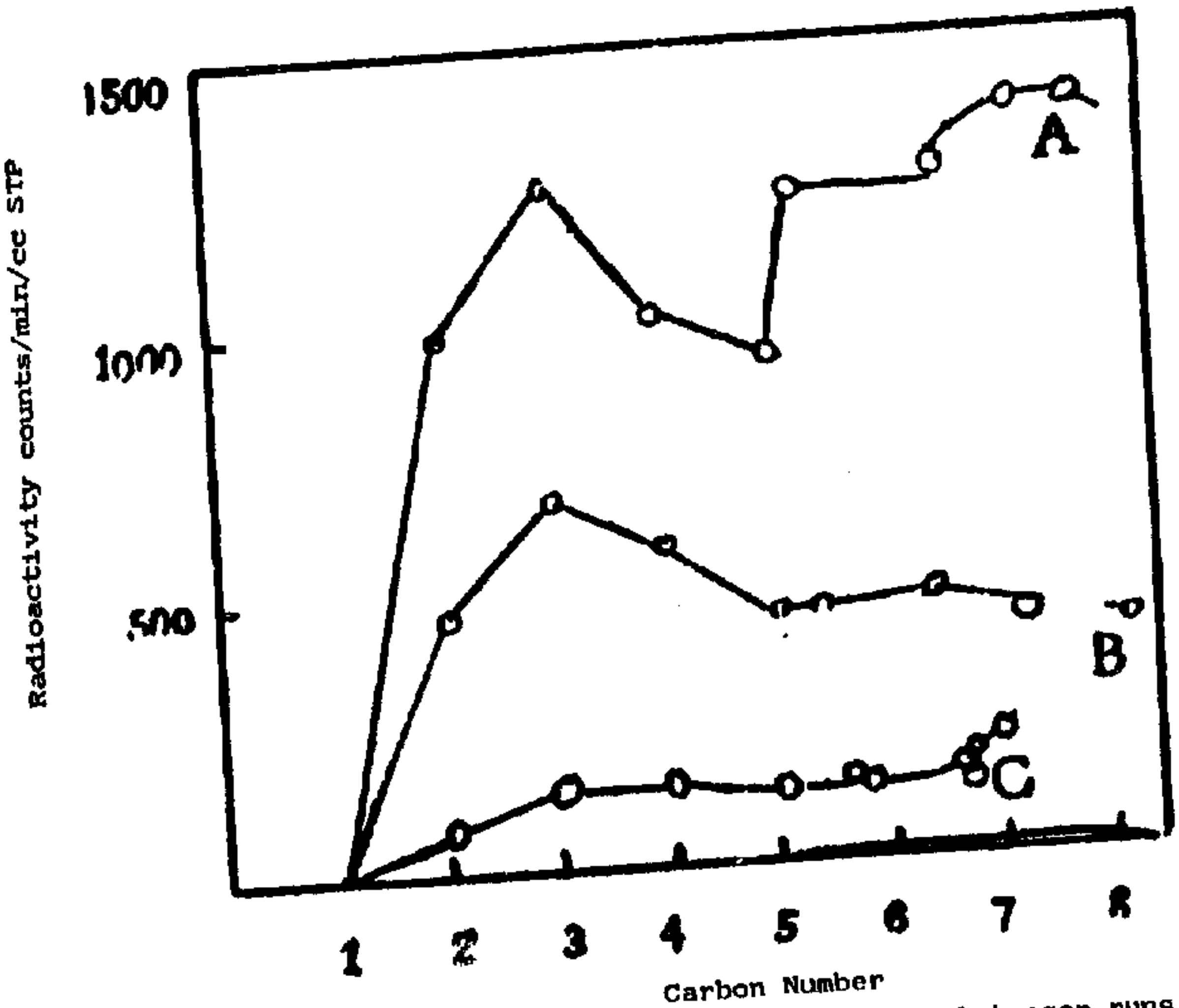


Figure I-8. Influence of pressure in ethanol tracer runs over doubly promoted iron catalysts, D3001: A; H7, atom 245-275°; B, H19, 7.5 atom 241°; C, H15, 21 atom, 242° (see reference I-17 for details).

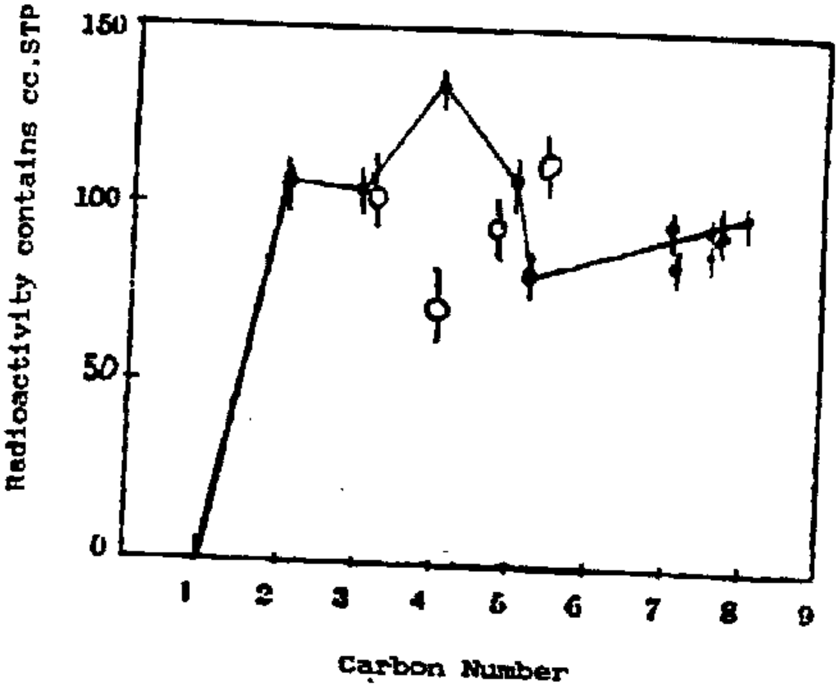


Figure I -9. Ethanol tracer runs over a nitrided iron catalyst at 7.5 atm. and 215°. The assumed precision of the data is indicated by the length of the vertical lines: O, alcohols; ●, hydrocarbons (from reference I-16).

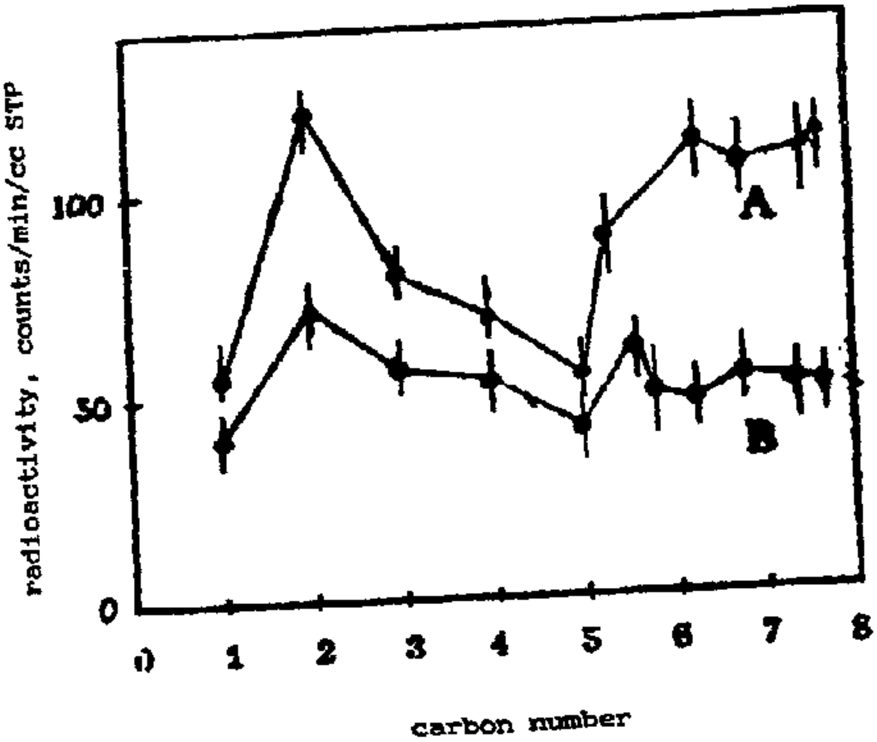


Figure I-10. Ethanol tracer runs over a cobalt catalyst. The assumed precision of the data is indicated by vertical lines. The activity of the ethanol in K13 was 75,000 counts/min/cc. STP; in run K16 it was 0080: A, K16 ethanol 1.5%; B, K13, ethanol 0.04%.

should be noted that direct hydrogenolysis of the C-O bond of the alcohol would produce a similar result.

Hall et al. (I-18) found that when a 50:50 H_2:CO synthesis gas containing 1.4% radioactive CO_2 was passed over an iron catalyst at 240°C, very little CO_2 was converted to CO, or to hydrocarbons. Thus, under these conditions the water gas shift reaction was slow. These workers also compared the results for the conversion of a syngas containing ^{14}C labeled methanol at 1 and 7.5 atm conditions. The data (figure I-11) generally show a similar trend at both pressures and indicate that the added methanol is incorporated in both the chain growth steps as well serving the principal function of initiating chains. Since methanol decomposed to produce ^{14}C labeled CO, the slope in the curves in figure I-11 arises from the normal chain growth by CO. The formation of CO from methanol, but CO_2 from the other primary alcohols, should be noted.

Hall et al. (I-18) also converted ^{14}C labeled formaldehyde at 1 atm and 230°C. The results were rather similar to those obtained with methanol at 1 atm conditions. They stated that the data do not preclude, and are consistent with, the formation by formaldehyde of a chain initiating complex with or without a chain-building complex.

Hall et al. (I-19) converted a 1:1 H_2:CO synthesis gas containing 1 to 1.25 mole % radioactive ethene with an iron catalyst at 224°C. About 12% of the hydrocarbons formed at 1 atmosphere stem from the added ethene but at 100 psi only about 6% of the hydrocarbons are formed from ethene. The catalyst used for atmospheric studies contained 0.64% Al_2O_3 and 2.00% ZrO_2 in addition to iron oxide; the catalyst for the 100 psi run was a doubly promoted iron catalyst containing 0.6% SiO_2, 0.6% Cr_2O_3, 4.6% MgO and 0.6% K_2O. The activity of methane was low, clearly showing that hydrocracking of polymers on the surface is not an important reaction. At atmospheric pressure, in the absence of added water, essentially all of the ethene reacted, the principal reaction being hydrogenation to form ethane. In the experiment at 100 psi with a doubly promoted iron catalyst, the incorporation of ethene to form higher hydrocarbons was only about 6%, about half that obtained with a singly promoted catalyst at 1 atm. More importantly, it was reported that in contrast to the one atmosphere runs, the activity fell off strongly with increasing carbon number.

These authors also converted ^{14}C labeled propanol with the singly promoted iron catalyst at 1 atmosphere conditions. The results showed that its behavior was quite similar to that of 1-propanol, with an incorporation of about 37%. In all respects, the data obtained with propanol were explicable with the assumption that the propanol adsorbed and formed the same complex as 1-propanol.

These authors (I-19) also put the combined alcohol data into a simple mechanistic picture as follows:

"The mechanisms proposed by Storch, Golumbic and Anderson (I-19) and by Kummer and Emmett (I-15) involved a type of adsorbed alcoholic complex. Ethylene could form such a complex by known reactions if it (a) hydrated to form ethanol or (b) underwent hydroformylation to 1-propanol. There is evidence that neither of these reactions occurred. If reaction (a) occurred

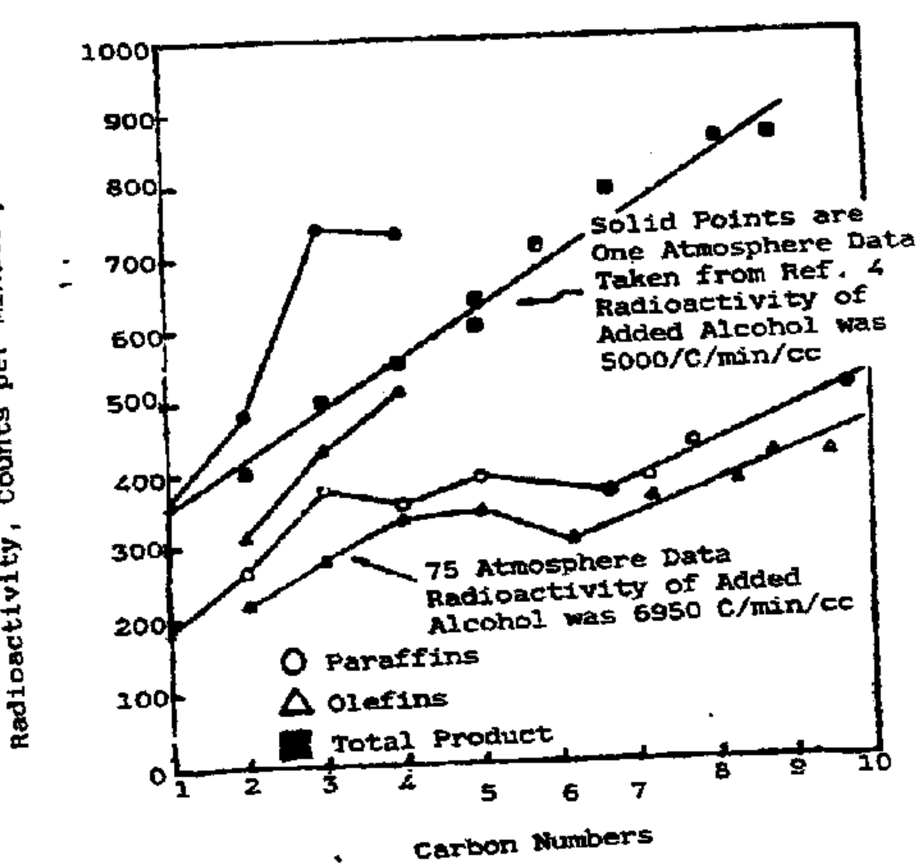


Figure I-11. Radioactivity of hydrocarbons obtained in the experiment in which 1% radioactive methanol was added to the synthesis at 7.5 atmospheres. These data are compared to the earlier one atmosphere results (from reference I-18).

in the ethylene experiments, it should also have occurred with the radioactive ethylene formed in the ethanol experiments. Thus, with methylene labeled ethanol

$$CH_2C^{14}H_2OH \rightleftarrows CH_2{=}C^{14}H_2 + H_2O \rightleftarrows C^{14}H_3 - CH_2OH$$

would be expected so that the position of the radioactive carbon relative to the hydroxyl group would have changed in a portion of the alcohol during synthesis. Examination of the unreacted radioactive ethanol, recovered from the products, showed that this had not occurred. If (b) occurred, the radioactivity distribution in the C_4 products should resemble that observed in 1-propanol tracer experiments, i.e., the activity of the branched C_4 hydrocarbons should be about 33% the activity of the straight chained hydrocarbons. Actually, the activity of the branched C_4 hydrocarbons was found to be 72% of the activity of the straight chain C_4 hydrocarbons. It appears, therefore, that the complex formed from adsorbed ethylene need not resemble the alcohol-type complexes suggested previously (I-2, I-15).

If ethylene does in fact form a different complex from that formed from ethanol, it becomes necessary to re-examine the alcohol experiments already reported (I-14, I-15, I-16, I-18). Let it be assumed that chain building complexes can be formed from adsorbed alcohols and that a different type of complex can also be formed from ethylene, but, for the moment, that other olefins do not form such complexes. In this situation, whenever a radioactive C_1 or C_2 alcohol is added to the synthesis, the resulting distribution of radioactivity in the products should be a weighted summation of those stemming from the alcohol and those from ethylene. Thus, for ethanol, by taking the value of the activity observed for the C_2 fraction as the contribution per mole to all hydrocarbons of higher carbon number and adding on the experimentally observed contribution from the ethylene, by proper weighting the qualitative features of the experimentally determined curves for both atmospheric and pressure runs can be reproduced. Similarly, methanol reacts to give radioactive C_2 complexes like those formed in ethanol tracer experiments. All C_{2+} hydrocarbons are formed via these C_2 complexes by addition of one or more radioactive chain building units. In this simple case the activity vs. carbon number curve should be calculable from the radioactivity of the chain-building complex and the actual data from an ethanol tracer experiment. Specifically, these activities should be those found in an ethanol tracer experiment plus $(n-2)\,\Delta$ where n is the carbon number and Δ is the activity of the chain building complex. In figure I-12, the calculated points are compared to the points for the experimental data obtained atmospheric pressure and at 100 psi. In each case, the "equivalent activity" of the ethanol was fixed by the activity of the C_2 hydrocarbons from the corresponding methanol tracer experiment. Likewise, the value of Δ was determined from the slope of the plot of the data at high carbon numbers. The agreement is quite good. It implies, of course, that the C_2 complexes formed from methanol are the same as those formed from ethanol but does nothing to define its nature.

If it is now supposed that propylene is also capable of build-in, similar to ethylene, when present in large concentrations, an explanation is available for the appearance of radioactivity in the iC_4 fraction when 1-propanol is added to the synthesis.