From the above it appears that the principal features of the Fischer-Tropsch experiments are explicable in terms of the mechanism suggested by Storch, Golumbic and Anderson (I-2) as modified by Kummer and Emmett (I-15). For a more detailed explanation of the results, however, it must be assumed that in addition to complexes formed on the surface by adsorption of alcohol, another formed from ethylene is also capable of "building-in", to form high molecular weight hydrocarbons.

In spite of the shortcomings of the simple picture developed through earlier work (I-14, I-15, I-16, I-18), the assumption that adsorbed alcohols are intermediates in the Fischer-Tropsch synthesis does explain many of the features of the tracer experiments with iron catalysts."

Blyholder and Emmett (I-20, I-21) conducted several experiments where methylene or carbonyl ^{14}C labeled ketene ($CH_2=C=O$) was added to the synthesis gas using a singly promoted iron catalyst (1.6% ZrO_2 and 0.58% Al_2O_3) or cobalt ($Co:ThO_2:MgO$:kieselguhr = 100:6:12:200) at atmospheric pressure. The results in figures I-13 and I-14 show that the products produced when methylene ^{14}C labeled ketene was added have essentially a constant molar activity; with iron the activities of the products are essentially the same as ketene whereas the products are only about one-third as active as the ketene when cobalt was the catalyst. The results show that the ketene functions to initiate chain growth but that neither ketene nor the CH_2 that could be formed from it serve for chain propogation. Also, the ketene is a much more effective chain initiation than either alcohol or alkene.

When carbonyl ^{14}C labeled ketene was added to the syngas quite different results were obtained (figures 1-15 and I-16). In this case, the activity increased with carbon number; furthermore, the linear plot extrapolated to the origin for zero carbon number. The data, together with the methylene labeled ketene, indicated that the ketene dissociated on the surface to produce adsorbed methylene, CH_2, which initiates chain growth and CO which serves as a source of carbon for chain growth. However, Toyoshima (I-22, I-23) later conducted work in Dr. Emmett's laboratory where samples were withdrawn at points along the length of the reactor provided data to cast doubt upon these ketene studies.

I-B-2. Schulz and Coworkers

The ^{14}C tracer studies by this group emphasized the conversion of labeled alkenes added to the synthesis gas, although some preliminary results from conversions in which labeled alcohols were added to the synthesis gas are reported.

Two ^{14}C labeled hydrocarbons were converted over a cobalt catalyst at 190°C and 1 atm pressure (Table I-1, ref. I-24). Both n-butane and 2-methylpentadecane were quite inert under these synthesis conditions; 1.0% or less of the alkane was converted. Hydrogenolysis was the dominant reaction.

^{14}C labeled ethene, propene and hexadecene were also converted over the cobalt catalyst (Table I-3, ref. I-24). In a detailed study with ^{14}C labeled ethene, Schulz and Achtsnit (I-25) found that the following reactions could be distinguished and identified: hydrogenation, chain initiation, chain growth, chain termination, oligimerization and hydrogenolysis. The

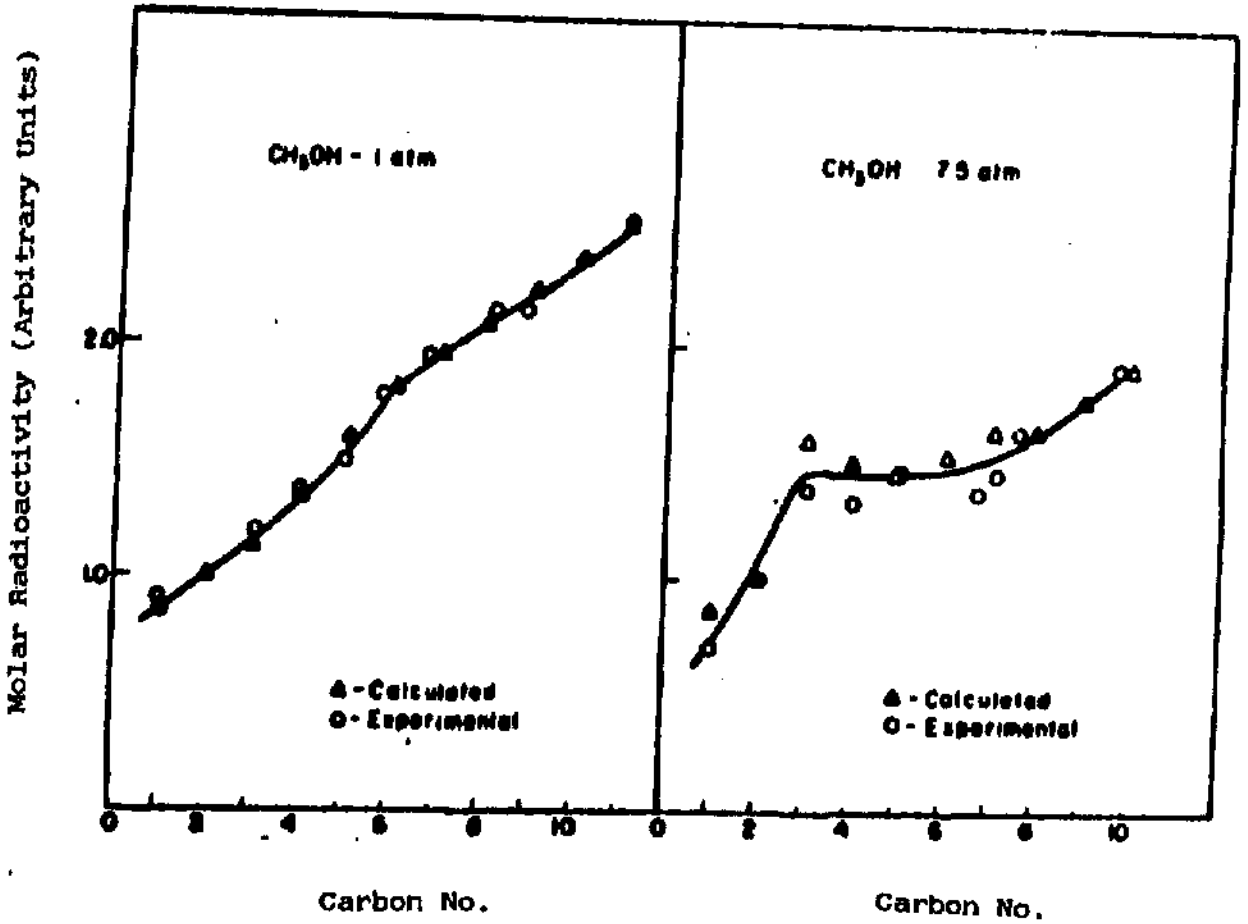


Figure I-12. Comparison of calculated and experimental data for methanol tracer runs (from reference I-19).

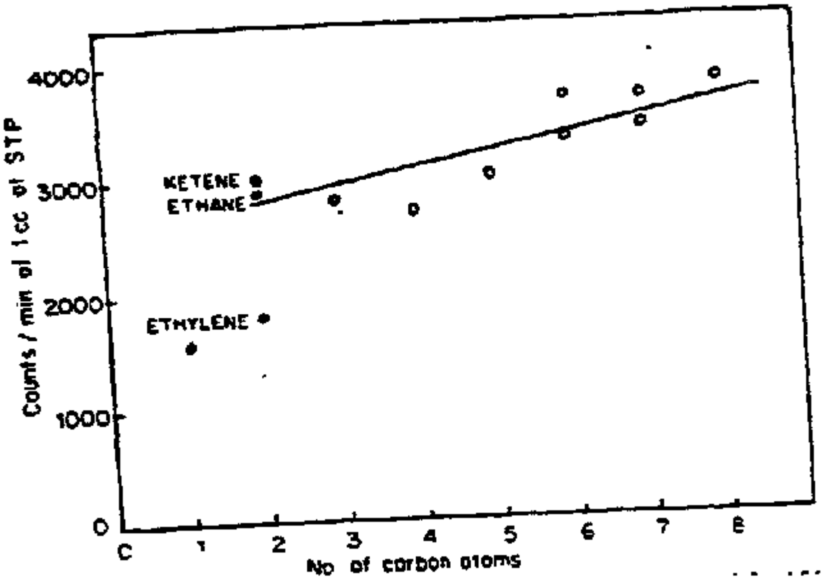


Figure I-13. Radioactivity of hydrocarbon product with 2% radioactive ketene added to synthesis gas passed over an iron catalyst at 247° and one atmosphere pressure.

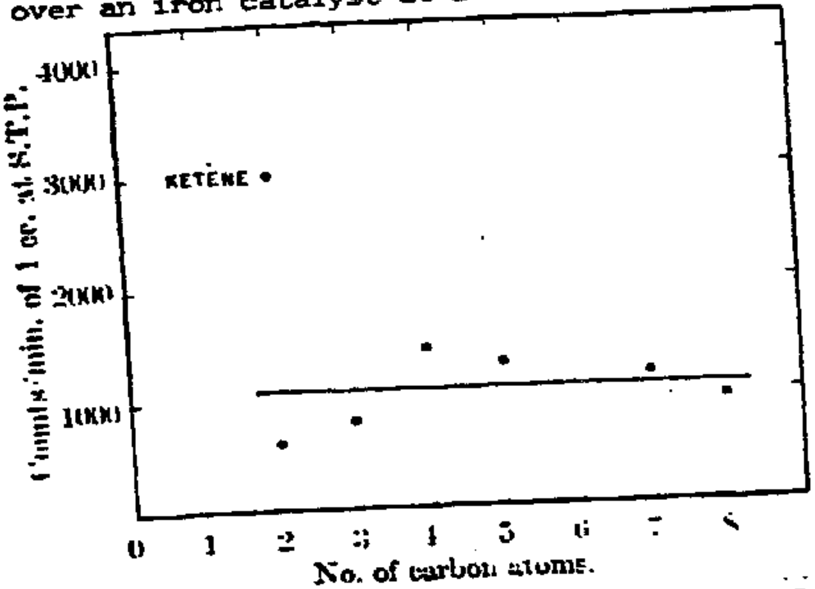


Figure I-14. Radioactivity of hydrocarbon product with 0.25% radioactive ketene added to synthesis gas passed over a cobalt catalyst at 185° and one atmosphere pressure.

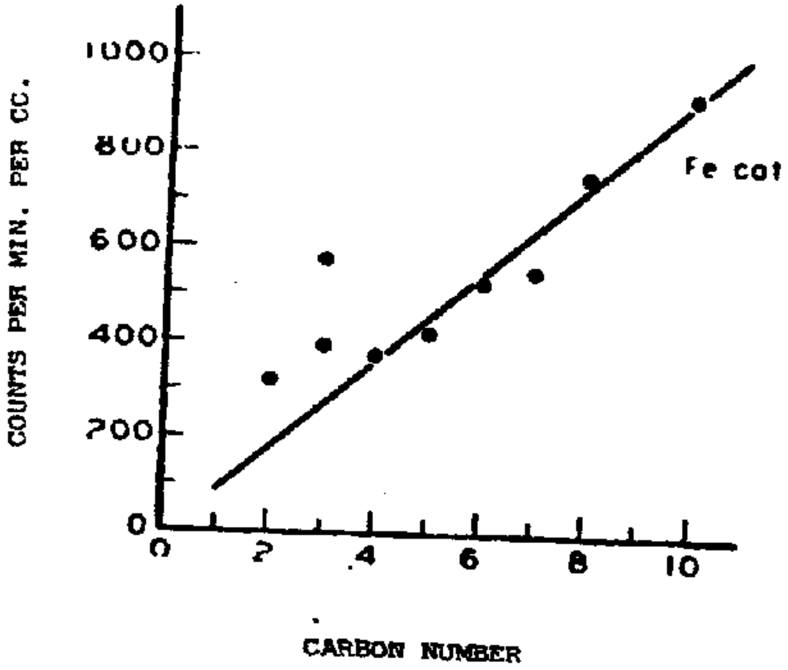


Figure I-15. Radioactive of hydrocarbons formed on adding 0.7% CH_2C^*O to 1:1 H_2:CO over a singly promoted iron catalyst.

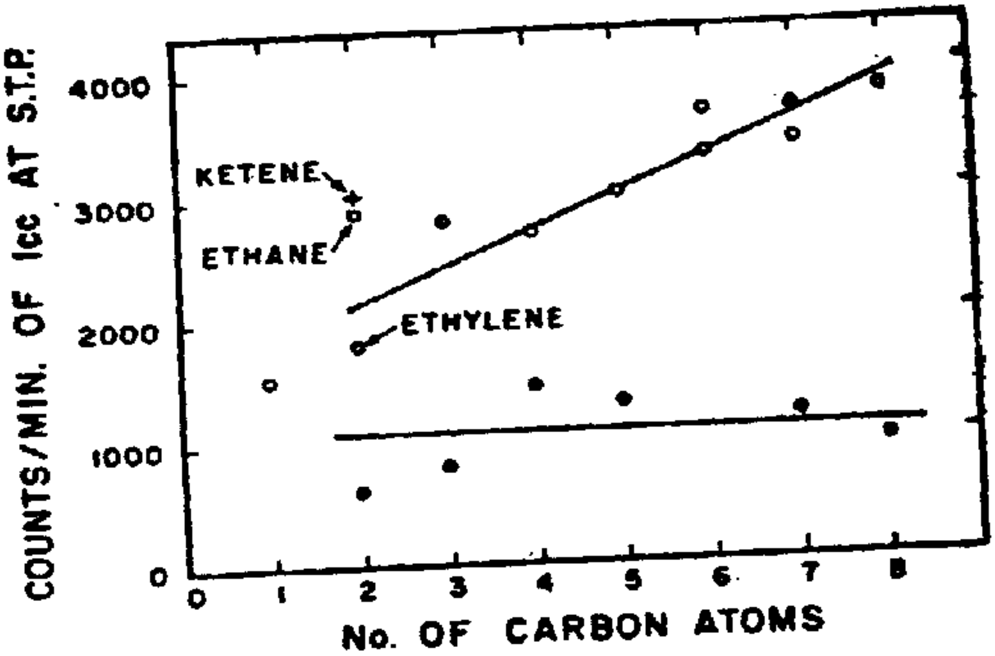


Figure I-16. Radioactivity of hydrocarbons formed on passing 2% radioactive ketene (3,000 counts per minute per cc. labeled in the methylene group) in a 1:1 $CO:H_2$ mixture over an iron catalyst at 240° (open circles) and passing 0.25% methylene labeled radioactive ketene in a 2:1 $H_2:CO$ mixture over a cobalt catalyst at 185 (solid circles).

selectivity for these reactions changes appreciably with reaction conditions using a cobalt catalyst.

Table I-3

Relative Ethylene-^{14}C Consumption for Chain Initiation, Chain Growth and Chain Termination in Dependence of H_2/CO Ratio of the Synthesis Gas

$H_2:CO$	1:1	2:1	4:1
Temperature, °C	187	187	187
Space Velocity, h^{-1}	89	85	88
Initiation, %	24.8	13.6	7.21
Growth, %	4.3	5.1	6.1
Termination, %	4.1	8.6	7.1
<u>Ratios:</u>			
Initiation/Growth	5.7	2.7	1.2
Initiation/Termination	6.1	1.6	1.0
Growth/Termination	1.1	0.6	0.8

The H_2/CO ratio in the synthesis gas was varied from 1:1 to 2:1 to 4:1. This resulted in 36, 72 and 99% conversion for CO and 95, 99.9, and 99.9% conversion of ^{14}C labeled ethene. The proportion of labeled ethene converted to methane increased with increasing H_2/CO ratio from 2.7 to 5.1 to 8.8%. The olefinic portion of the hydrocarbon products decreased with increasing H_2/CO ratio. For ethene, the amount of the labeled compound that was hydrogenated to labeled ethane was 66.6, 70.6 and 71.7%, respectively. The amount of ^{14}C in products C_2 plus was 20 to 30% for the three experiments. This incorporation into C_2 products may occur by three processes: chain initiation, propagation, or termination.

One run with ^{14}C labeled ethylene was described in detail (Figure I-17, ref. I-25, I-26). The slope of the linear part of the curve in the higher carbon numbers (C_7-C_{12}*) shows the increase of the molar activity due to chain propagation; extrapolation of this line to C_2 gives the starting point for the run with ethene tracer. The horizontal (to the carbon number axis) line through this C_2 point indicates the amount of molar activity in each carbon number fraction that originates from chain initiation. Finally, the fraction of ethylene incorporation due to chain termination is the difference between the experimental curve and the straight line defined by chain growth incorporation. The data in figure I-17 indicate that chain termination by ethene is insignificant for those surface species that lead to C_6 and higher carbon number products. The relative amounts of ethene incorporated into C_2 plus products are summarized in Table I-4.

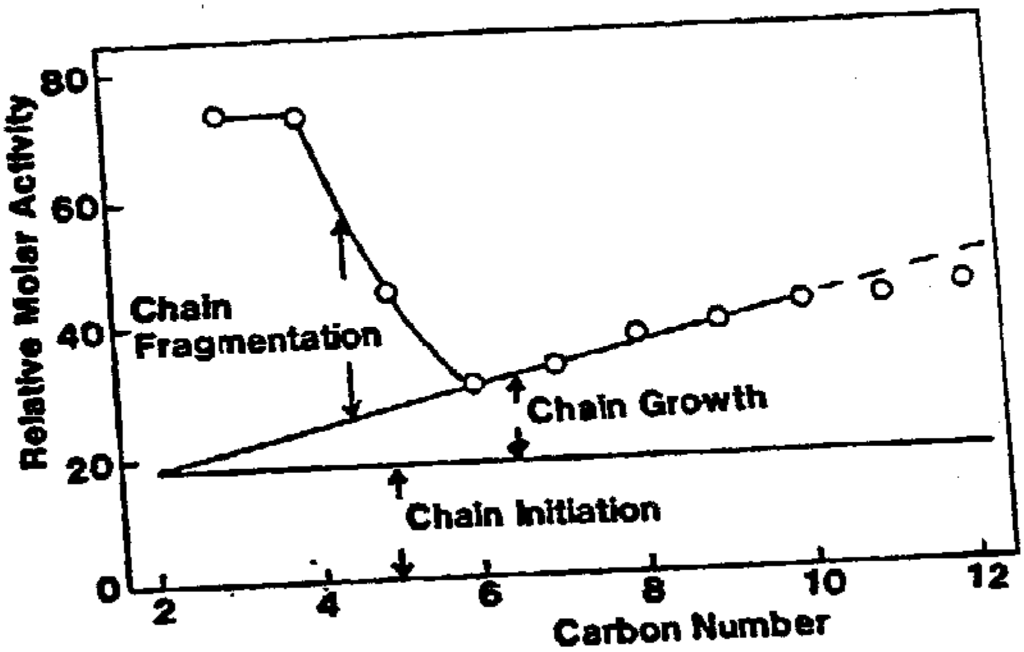


Figure I-17. Relative molar activity in the products from syngas conversion with added ethene[^{14}C] using a cobalt catalyst at atmospheric pressure.

Table I-4

Ethylene-^{14}C Reaction During the Fischer-Tropsch Synthesis in Dependence of Reaction Temperature and Space Velocity

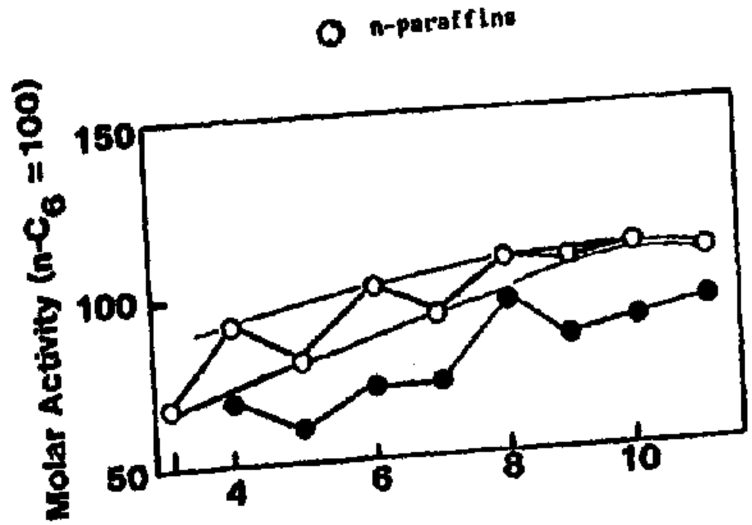
H_2:CO	2:1	2:1	2:1	2:1
Temperature, °C	171	187	208	190
Space Velocity, h^{-1}	87	85	80	251
Ethylene-^{14}C Conversion, %				
Total:	99.5	99.9	99.9	99.9
to ethane	72.3	70.6	55.6	62.3
to methane	1.2	5.1	18.0	2.9
to products C_3^+	26.0	24.3	26.3	34.7
Initiation/Growth	very lg.	2.7	3.8	2.8
Initiation/Termination	8.9	1.6	1.3	1.8
Growth/Termination	---	0.6	0.4	0.6

Another unique feature of ^{14}C labeled ethene incorporation into even carbon number products is illustrated in figure I-18. The n-paraffins (the data shown correspond to the total n-products since the hydrocarbon products were hydrogenated prior to analysis) have a higher activity than the odd carbon number compounds. This was taken to indicate that ^{14}C ethene undergoes oligimerization; thus, the extent that the activity of the even carbon number products exceed those of the odd one is a relative measure of the amount of oligimerization.

The role of temperature and space velocity upon ethene incorporation is illustrated in Table I-5 (next page). At the lower temperature methane formation is reduced to a very small value and chain initiation is essentially the only reaction of ethene incorporation into higher carbon number products. Increasing the temperature increases the extent of hydrogenolysis and the formation of branched compounds; the average molecular weight of the products is lowered with temperature increases.

These results with ^{14}C labeled ethene are very informative; however, one must note that the conversion of the labeled ethene is quite high. Thus, 95% or greater of the added ethene is converted to products. This provides great opportunity for a variety of secondary reactions to mask the initial reactions that ethene participates in.

^{14}C labeled propene was also converted with the cobalt catalyst. In the relative participation in the various reactions, it resembled ethene (Table I-3). However, there were noticeable differences. Perhaps the most striking is illustrated in figure I-19. The monomethyl paraffins have appreciably higher activity than the normal paraffins when labeled propene is incorporated; this is opposite to that observed when labeled ethene was incorporated (compare figures I-18 and I-19). Schulz and Achtsnit (I-25)



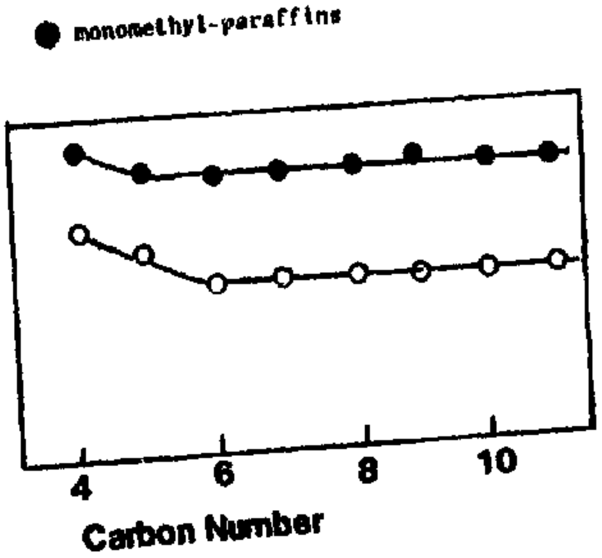


Figure I-18. LEFT Molar activity of the hydrogenated synthesis product as a function of the carbon number in the cobalt normal pressure synthesis with the addition of ethene [^{14}C] to the synthesis gas.

Figure I-19. RIGHT Molar activity of the hydrogenated synthesis product as a function of the carbon number in the cobalt normal pressure synthesis with the addition of propene [1-^{14}C] to the synthesis gas.

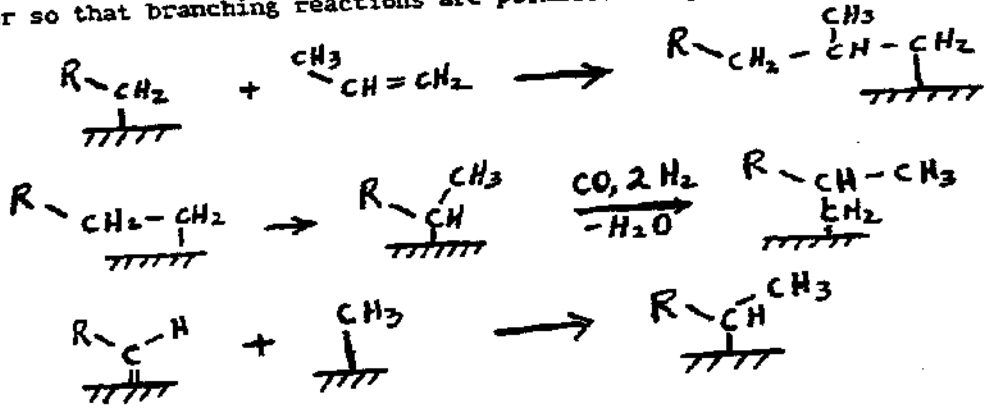
Table I-5

Tracer Studies to Elucidate the Mechanism of CO-Hydrogenation

A) Cobalt, 1 atm pressure, 100 Co/100 Kieselgur/18 ThO_2, 185 to 190°C, $CO:H_2$ = 1:2, space velocity 75 hr^{-1}

Tracer	Tracer Content in Synthesis Gas Vol. %	Tracer Transformation % ^{14}C of Input Total	Hydrogenation	Build-In	Hydrogenolysis	Hydrogenation to CH_4
Ethylene-^{14}C	0.30	99.99	66.7	29.0	4.3	4.3
Propene-1-^{14}C	0.29	93.7	50.9	31.1	11.7	9.2
Propene-2-^{14}C	0.78	93.1	52.0	31.3	9.8	6.4
Hexadecene-1-1-^{14}C	0.10	99.8	79.4	6.3	14.1	3.7
n-Butane-1-^{14}C	0.29	1.0	----	0.5	0.1	0.1
2-Methylpentadecane-15-^{14}C	0.23	0.7	----	0.25	0.45	0.15
B) Iron fixed bed, alkali precipitated catalyst, 220°C, 20 atm, $CO:H_2$ = 1:2, space velocity 80 hr^{-1}						
Ethylene ^{14}C	0.21	76.6	67.4	9.1	0.1	0.1
Propene-1-^{14}C	0.30	44.1	42.2	1.1	0.6	0.06
C) Iron, fixed bed alkali fixed catalyst, 320°C, 20 atm space velocity 450 Hhr^{-1}						
Ethylene ^{14}C	0.34	77.1	65.0	11.5	0.6	0.6

contend that as R becomes longer the steric hindrance for substitution becomes greater so that branching reactions are permitted only for "small species":



[I-4]

Thus, a steric effect is imposed to account for the different modes of additions of ethene and propene as demonstrated in figures I-18 and I-19.

A higher carbon number olefin, 1-hexadecene, was also used as a labeled tracer molecule with the cobalt catalyst. As the carbon number increased from 2 to 16, the fraction converted to alkane increased, the extent of incorporation into higher products decreased (about 30% for ethene and 6.3% for hexadecene) and the fraction undergoing hydrogenolysis (or another type of splitting reaction) increased (4.3% for ethene and 14.1% for hexadecene).

The molar activities of products from the conversion of synthesis gas with ^{14}C labeled 1-hexadecene are shown by carbon number in figures I-20 and I-21. The distribution of the splitting products from 1-hexadecene were remarkable. The label on the C-1 atom produced, in analogy with the results with propene-1-^{14}C and propene-2-^{14}C, methane ^{14}C as the main splitting product. Hexadecene produced, in addition to methane, larger amounts of radioactive products in the range C_2 to C_{15}; these could not be explained by a simple splitting of the radioactive hexadecene molecule nor could they be accounted for by assuming a partial double bond shift in the hexadecene molecule before the splitting.

The molar activity of the C_{15}^- products increase with increasing carbon number (I-28). The explanation given for this was that the hexadecene molecule formed a smaller grouping that contains the terminal ^{14}C atom that transforms to a smaller growing chain on the catalyst surface. The molar activity of the C_{16}^- branched compounds was lower than the corresponding normal compounds; by analogy to the products when ^{14}C labeled ethene or propene was added it was inferred that the propagating group had to be less than C_3. Furthermore, it was believed that when the propagating group was a C_1 unit there should be no difference in the activity of the normal and branched products. The authors therefore concluded that the propagating group is a C_2 unit comprised of the C_1 and C_2 carbons of the added hexadecene and that this group is common to other propagating groups on the catalyst surface.

The constant molar activity for C_{17}^+ products shows that 1-hexadene serves to initiate chain growth.

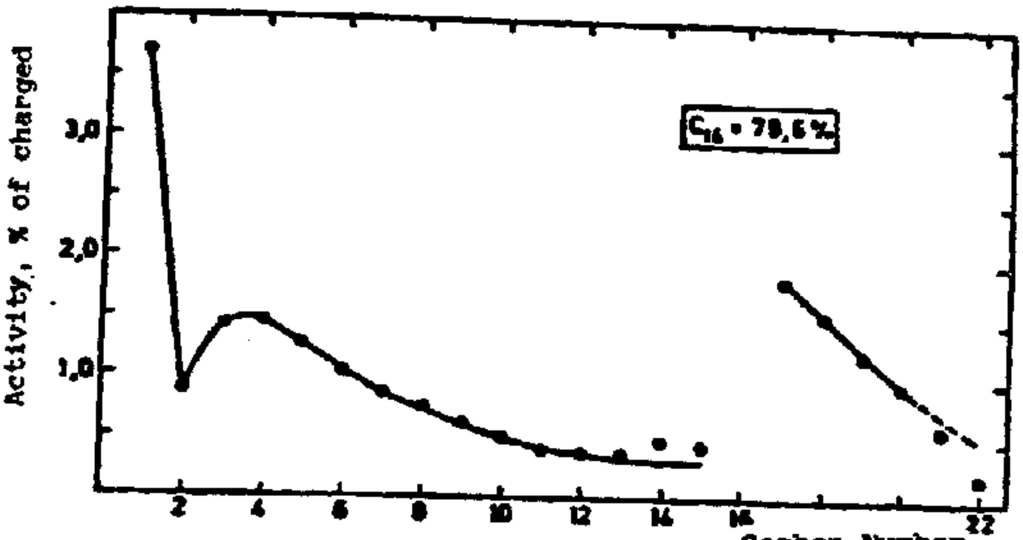


Figure I-20. Radioactivity distribution in the synthesis products. Conversion with 0.1 Vol. % 1-hexadecene-1-^{14}C in the synthesis gas, Co normal pressure synthesis.

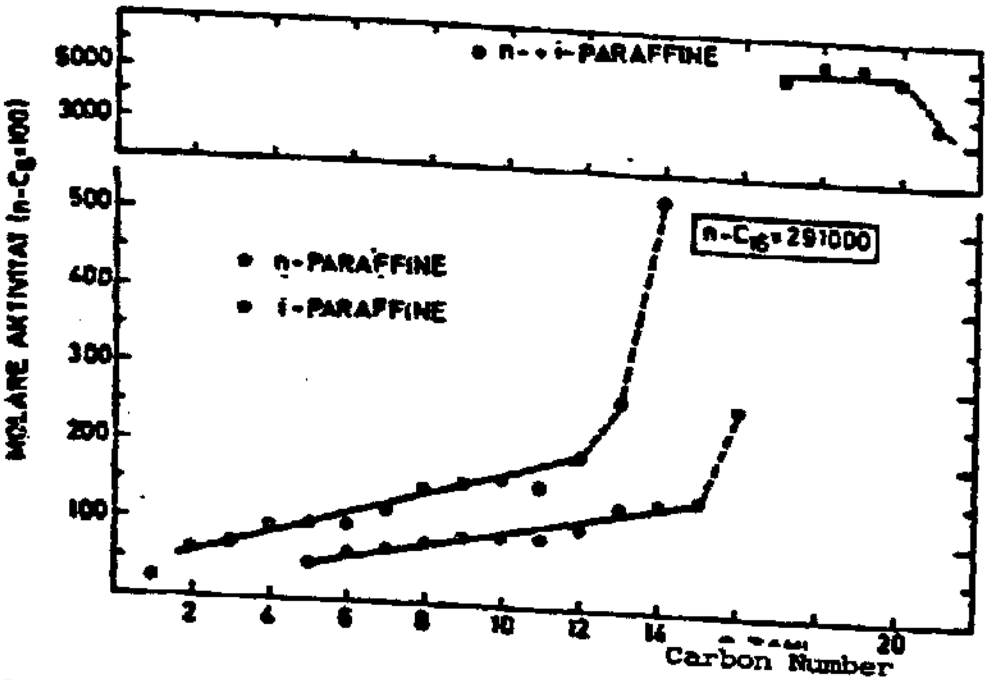


Figure I-21. Molar activity of the synthesis product (after hydrogenation); conversion of 0.1 Vol. % 1-hexadecene-1-^{14}C in synthesis gas, Co normal pressure synthesis.

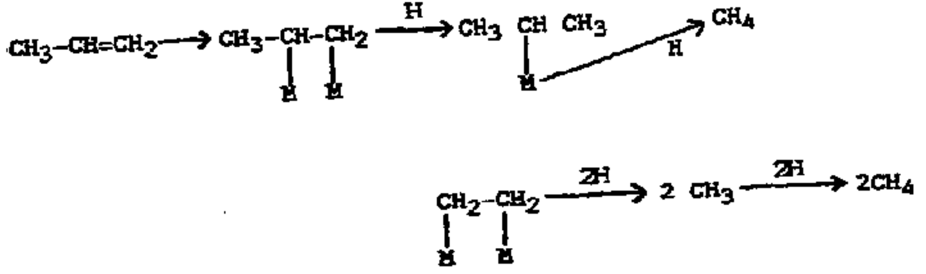
Results were also obtained for the conversion of syngas containing ^{14}C labeled ethene or propene using a precipitated promoted catalyst. In addition, a fused iron catalyst was employed in a run with labeled ethene at 20 atm pressure. They found that the cracking reaction of ethene was of secondary importance with the iron catalyst, unlike the case with cobalt. The distribution of the synthesis products from ^{14}C-ethene showed that about 50% of the transformation was to the C_3 product; the transformation to higher hydrocarbons decreased much quicker than for the cobalt normal pressure synthesis (figure I-22). With the addition of ^{14}C-ethane the iso-paraffins had a lower activity than the normal paraffins; this is consistent with the data for cobalt (figure I-23).

With the iron catalyst, ^{14}C-propene gave a somewhat higher splitting than ^{14}C-ethene. The propene-1-^{14}C transformation to C_3^+ hydrocarbons is low; the principal selectivity was for lower carbon compounds (figure I-24). Dimerization of propene-1-^{14}C occurred to produce 2-methylpentane with a much higher activity than either the i-C_5 or i-C_7 alkane. For normal hydrocarbons, butane has a much higher activity than the higher carbon number alkanes.

Pichler et al. (I-27) concluded that, for synthesis with a cobalt catalyst, olefins and carbon monoxide were to be regarded as interchangeable ligands of surface complexes, which are generally capable of undergoing the reaction of chain growth with alkyl ligands.

Schulz et al. (I-28, I-29) observed that during the cobalt normal-pressure synthesis isopropanol and acetone tracer compounds were interconverted by fast hydrogenation/dehydrogenation reactions; thus, both acetone and isopropanol initiated chain growth. With either acetone or isopropanol, propane was found to be one of the major products.

Schulz et al. (I-30) found, from studies with propene-1-^{14}C and propene-2-^{14}C, that successive demethantion of propene occurred and offered the following scheme to account for this (M represents catalyst surface site):



$$CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\underset{M}{\underset{|}{CH}}{-}\underset{M}{\underset{|}{CH_2}} \xrightarrow{H} CH_3\ \underset{M}{\underset{|}{CH}}\ CH_3 \xrightarrow{H} CH_4$$

$$\underset{M}{\underset{|}{CH_2}}{-}\underset{M}{\underset{|}{CH_2}} \xrightarrow{2H} 2\ CH_3 \xrightarrow{2H} 2CH_4$$

[I-6]

Schultz (I-31, I-32) has recently summarized how the results from his tracer studies can be incorporated into the overall view of Fischer-Tropsch synthesis.

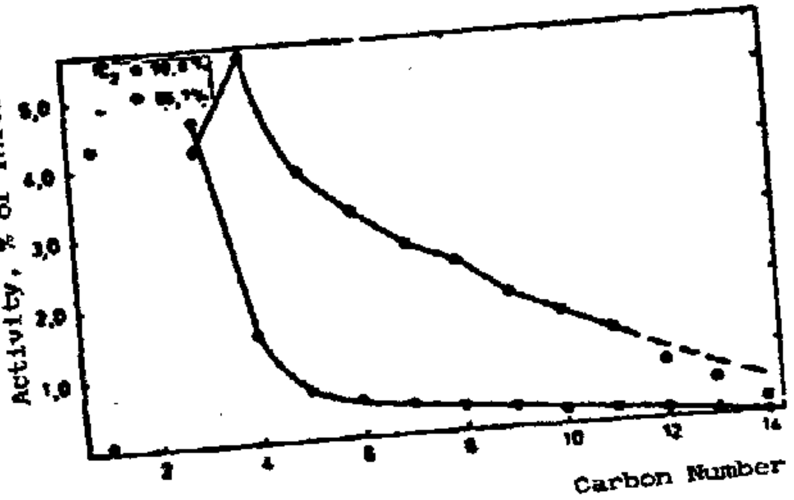


Figure I-22. Radioactive distribution in synthesis product, conversion of ethene-^{14}C in synthesis gas.

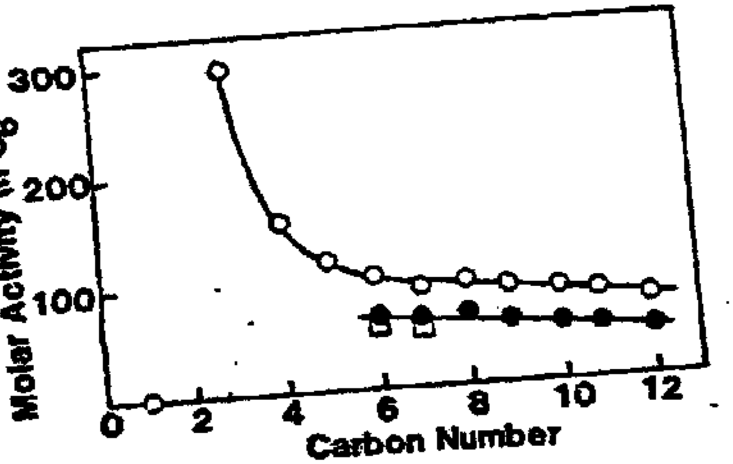


Figure I-23. Molar activity the synthesis product as a function of carbon number for the iron synthesis with the addition of ethylene [^{14}C] to the synthesis gas (relative molar activity of the C_2 product fraction 5040).

● monomethyl-paraffin

○ n-paraffin

□ 2-methyl-paraffin

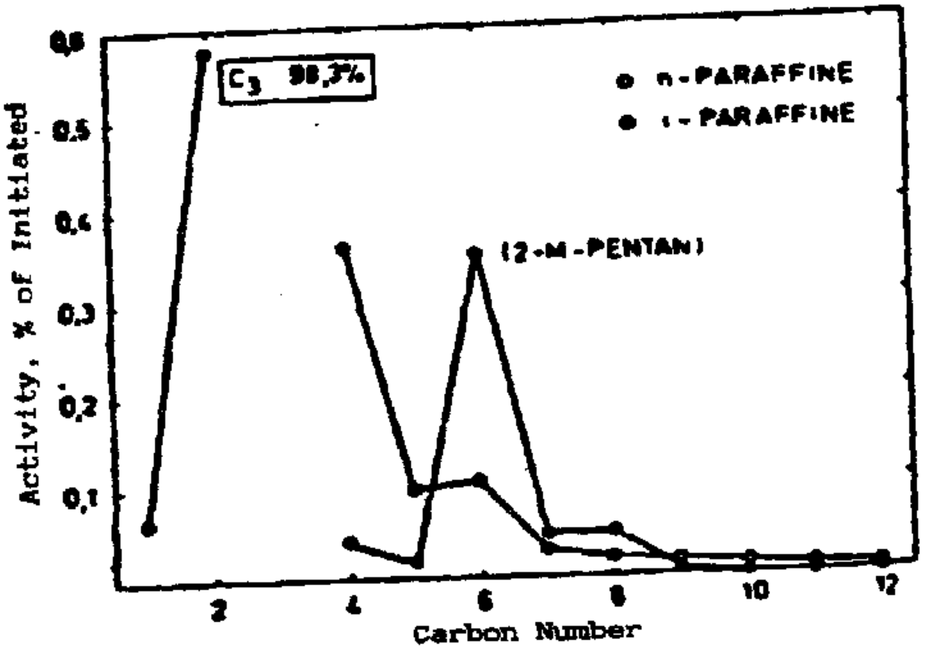


Figure I-24. Molar activity of the reaction product (after hydrogenation); conversion of 0.3 Vol. % propene-1-^{14}C in synthesis gas, iron medium pressure synthesis.

I-B-3. Other ^{14}C Tracer Studies

Two other ^{14}C tracer studies merit mention. Fletcher and Gibson (I-33) converted ^{14}C labeled CO in a mixture that consists of 5% CO with the remainder consisting of about equal amounts of ethene and hydrogen. The synthesis was conducted at 185°C and atmospheric pressure with a "supported and promoted" cobalt catalyst. About 60% of the CO reacted, and almost all of the ethene, of which about 50% was hydrogenated to ethane.

The gaseous products were separated and a pure propene fraction collected. This sample was degraded to produce CO_2 representing each carbon position; the relative activity in each portion was:

	CH_2 =	CH –0	CH_3
activity cpm/ml	304	26.5	220
relative activity	11.5	1.0	8.3

It was assumed that the activity in the middle carbon was uniquely derived from normal Fischer-Tropsch synthesis from CO. It was further assumed that the activity in the methyl position, after correcting for the propene synthesized directly from CO, was formed by an isomerization

$$CH_2 = CH - CH_3 \rightleftarrows {}^{*}CH_3 - CH = CH_2$$

With these two assumptions, the original activity distribution is then:

	CH_2 =	CH –	CH_3
activity, cpm	471	0	0

If this is so, it follows that CO reacts to form propene by direct addition to an ethene molecule.

The specific activity of the $C_3 - C_{12}$ fractions produce a straight line when plotted against carbon number (figure I-25). There were small, but barely significant, differences between the activities of the alkanes and alkenes of a given carbon number; the values plotted are the weighted mean of the two. It is obvious that the specific activity increases regularly with increase in carbon number. The rate of increase in activity is 550 cpm per carbon atom. The activity of the CO in the inlet gas was 3650 cpm per ml so that one atom in every 6 or 7 is derived from CO. While the results reported in reference I-33 are interesting, they were obtained under conditions that are far removed from normal synthesis conditions.

Roginskii (I-34) added ^{14}C labeled ethanol to a syngas feed to a cobalt catalyst under atmospheric pressure conditions. His results were similar to those reported by Emmett and coworkers.

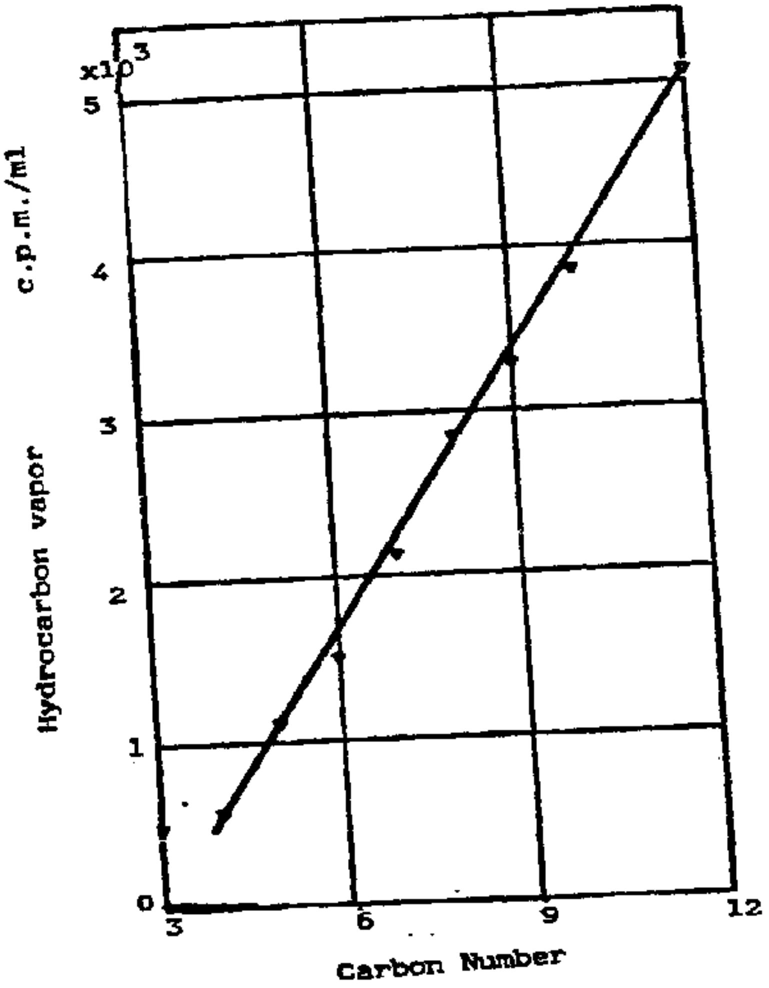


Figure I-25. Variation in radioactivity with carbon chain length.

I-B-4. Other Tracer Studies

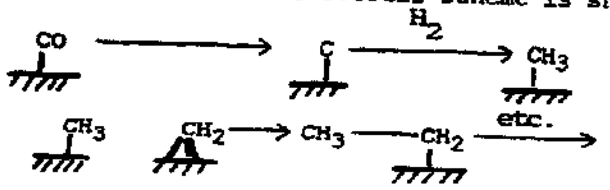
For the most part ^{13}C has been used to conduct isotopic transient studies. Many of these studies have been conducted with methanation catalysts; a typical study is outlined by Biloen et al (I-35). A detailed consideration of the technique and much of the data generated in these studies has been provided recently by Hapel (I-36). For the most part these studies have not utilized iron catalysts. In some few instances the ^{13}C isotopes are utilized in studies similar to those previously outlined for ^{14}C. For example, Bell and coworkers (I-37) have utilized ^{13}CO with ethene to determine the extent of olefin incorporation in Fishcer-Tropsch synthesis using a Ru catalyst.

An exception is the Exxon group who have utilized the transient method with an iron catalyst at ca 0.01 atm. pressure (I-38). The iron catalyst was promoted and conditions were chosen to maximize the selectivity for terminal alkenes. In addition products were trapped and n.m.r. was utilized to learn the ^{13}C isotope distribution in certain products. By examining both the rate and position of new label incorporation (Figure I-26) they were able to show that the major fraction of hydrocarbon products at steady state is derived from a much smaller number of growing chains than previously thought. Their data placed a lower limit to the average rate of chain growth in the system to two to four bonds per second. The ^{13}C distribution in the 1-butene product was, within experimental error, isotopic. Thus, the collected butenes must have grown in a much shorter time than the time in which the isotopic composition of their surface precursors changed appreciably. They estimated that at steady state fewer than 50 mmol of growing chains per gram of catalyst were responsible for over half of all the C_2^+ hydrocarbon product. Mims et al (I-39) did similar experiments with Ru catalysts (Figure I-27).

Brady and Pettit (I-40) utilized ^{13}C labels diazomethane (CH_2N_2) as an additive to the syngas feed to a CO catalyst. They outlined three mechanisms as described below:

"...The first, proposed by Fischer and Tropsch in 1926 I-41), suggested that the C-C bonds of the product are produced via polymerization of CH_2 fragments on the metal surface. Through reaction of CH_2N_2 under conditions of the reaction, we have recently indicated that in the presence of H_2 methylene groups do polymerize on such metal surfaces to produce linear hydrocarbons, and the data indicate that the growth occurs via insertion of a surface CH_2 species into a metal-alkyl bond to generate the next higher homologous alkyl ligand (I-42).

The essence of the overall scheme is shown in eq [I-7].



[I-7]

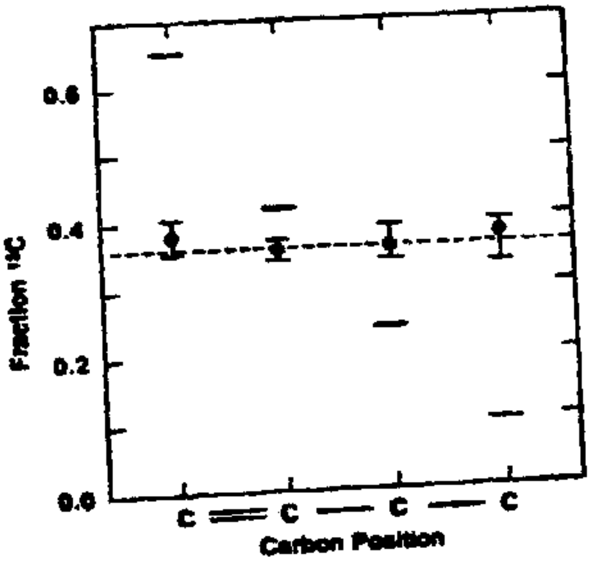


Figure I-26. Fraction of ^{13}C at each position in the traniently labeled butene sample. The dashed horizontal line is the average value derived from GC/MS analysis. The short horizontal lines illustrate the anisotropy that would have resultd it only ^{13}C had been added sequentially to one end of the growing chains (from reference I-38).

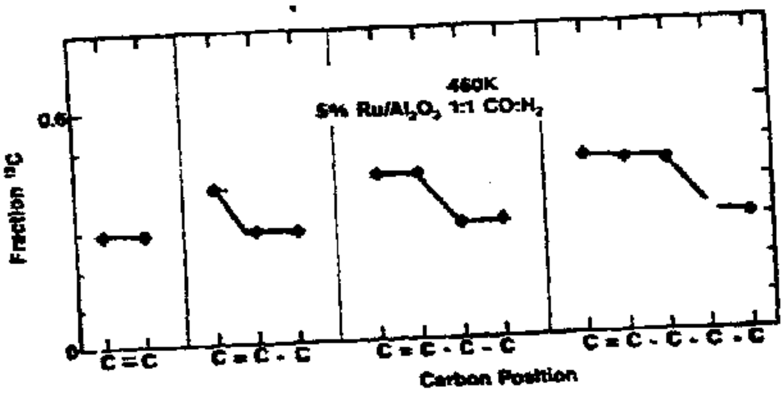
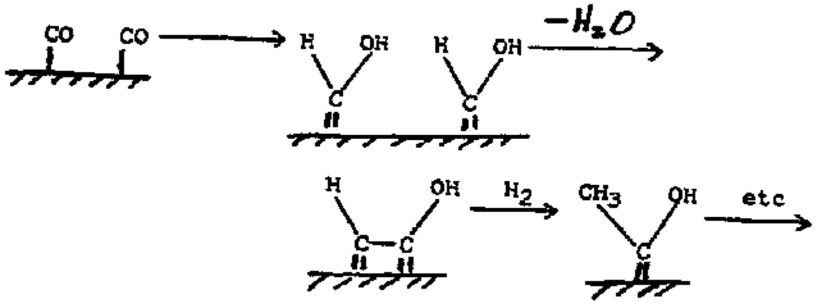


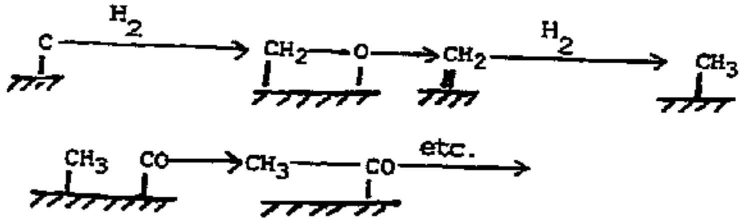
Figure I-27. Proton NMR results for the C_2-C_5 products trapped between 4 and 24 seconds after the switch from ^{12}CO to ^{13}CO (from reference I-39).

A second mechanism advanced by Anderson and Emmett and their co-workers (I-2, I-15) suggested that the C-C bonds are made through a condensation reaction involving loss of H_2O between hydroxy methylene groups on the surface (eq [I-8]).



[I-8]

The most recent scheme, advanced in 1970 by Pichler and Schultz (I-24) and subsequently given with minor variations (I-43, I-44), suggested that the C-C bonds arose through insertion of CO into metal-alkyl bonds in homogeneous systems. The scheme is given in eq (I-9); of importance to the present work is that the initial metal-methyl bond is proposed to arise through reduction of a surface-bound CH_2 species.



[I-9]

These authors obtained linear ASF plots (Figure I-28). The change in the slope from 0.24 to 0.51 indicates that the rate of propagation, relative to termination, increased by a factor of 3.3 upon addition of CH_2, and hence CH_2, to the surface. It should be noted that the value of the slope, even with added CH_2N_2, is much lower than is usually obtained with cobalt catalysts. These authors also determined the ^{13}C distribution in the propene product. From this data, the authors concluded that only the sequence of steps outlined in equation [I-9] can be considered as the primary mechanism of the Fischer-Tropsch reaction.

I-C. Outline of Proposed Research

The proposed research will utilize a kinetic isotope method (KIM) to explore the role of promoters in altering chain initiation and/or growth for iron Fischer-Tropsch catalysts. This method was used in studies by Emmett and coworkers (I-14 through I-22) in the 1950-60's. He was able to demonstrate that some compound classes were rather inert in the synthesis conditions while other compounds served to initiate chain growth. In the present study several compound classes will be utilized in the KIM studies. Both low (1-2 carbon) and higher (5-10 carbon) molecular weight compounds will be included in this study.

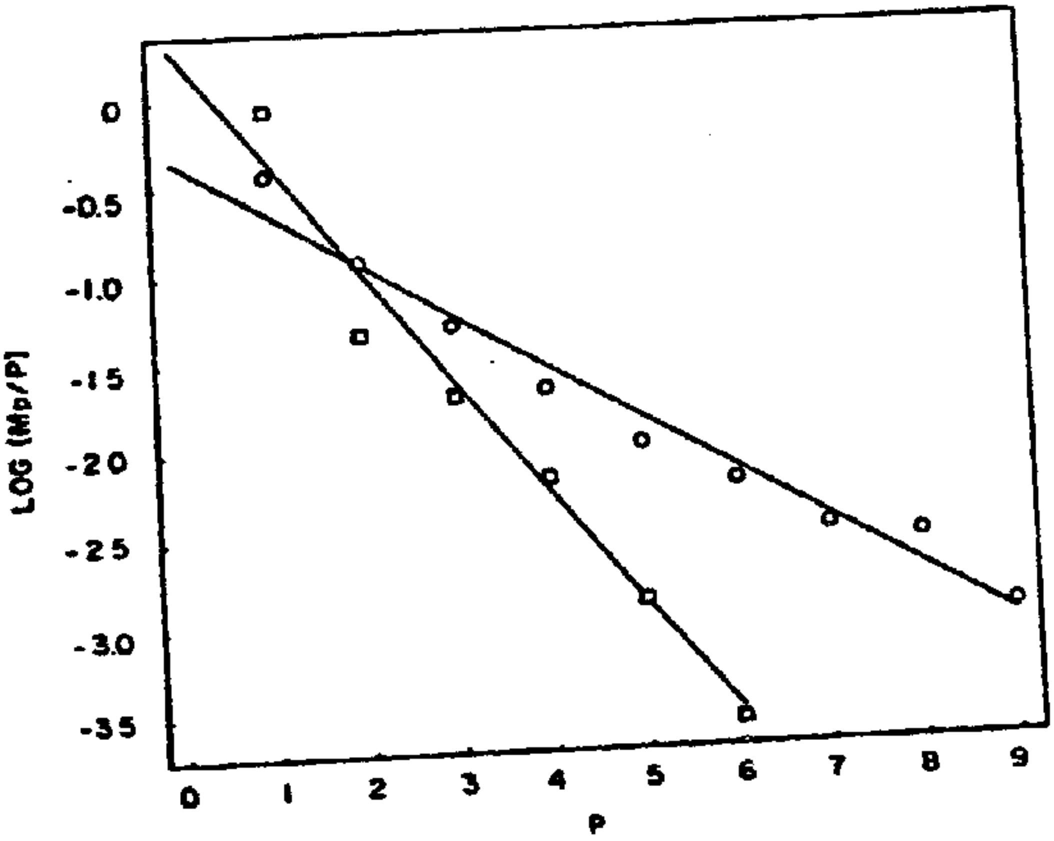


Figure I-28. Plots of log (M_p/P) vs. P for the distribution of oligomers produced when CO and H_2 (○) and $CO + H_2 + CH_2N_2$ (□) are passed over a cobalt catalyst. The lines represent the least-squares fit for the data. The values (see text) for the $CO + H_2$ data are 0.23 (ex. slope) and 0.25 (ex. intercept) and for the $CO + H_2 + CH_2N_2$ data are 0.51 (ex. slope) and 0.51 (ex. intercept) (from reference I-40).

Initial runs will be a commercial catalyst (C-73 from United Catalysts, Inc.). This catalyst has been chosen (i) because it has been utilized in detailed activity and selectivity studies by PETEC and MIT investigators and (ii) the cooperative studies in catalyst characterization by UCI and IMMR personnel Both PETEC and MIT workers have described similar experimental arrangements utilizing a stirred tank reactor and appropriate product collection vessel. They have also outlined analytical procedures for gaseous and for both aqueous and organic liquid samples. These procedures will be followed for our quantitative analysis.

The experimental program to follow the base-line work with C-73 catalyst is outlined below:

Test Series	Alkali Promoter	Structural Promoter
1	None	None
2	Potassium or calcium at optimum concentration	None
3	None	Alumina
4	Vary potassium from low high (ca. 3wt. %)	Constant alumina loading
5	Optimum potassium concentration	Vary alumina
6	Optimum potassium concentration	Vary oxides which are selected according to base strength
7	Vary alkali and alkali earth	Constant structural promoter

Catalyst preparation studies will be carried out while doing the base-line catalyst studies. Preparation procedures for adding promoters will involve: (1) impregnation of iron oxide derived from precipitation, (2) impregnation of a commercial iron oxide catalyst base, (3) coprecipitation and (4) by sequential or co-impregnation of a high area support. These catalyst formulations will be evaluated for activity and catalyst stability using unlabeled feed and fixed bed, plug flow reactors. The selection of a preferred catalyst preparation procedure for the tracer work will be done on the basis of the results of these studies.

A catalyst will be brought to steady-state conditions in unlabeled reactor feed. At this point a series of labeled compounds will be added to the feed; these compounds will be utilized one at a time separated by intervals of operation with unlabeled feed.

Products from the operating periods will be analyzed by high resolution gas chromatographic techniques. Carbon-14 content of products obtained from operating periods with labeled intermediates injection will be determined using a gas proportional counter in series with a thermal conductivitydetector gas chromatograph. Because of counting difficulties encountered with low level labeled products, packed columns will be required for the C-14 analysis. Thus, the peak resolution will be poorer than for the capillary or tubular g.c. columns because of the packed column and because of the tube volume between the g.c. and the proportional counter as well as the large volume of the proportional counter. Figure I-29 illustrates results that we have obtained with C-14 gas radiochromatographic analysis for a sample from the conversion of a light naphtha doped with methyl [1-^{14}C] cyclohexane. A Carbowax packed column gave excellent separation of aromatics but poor separation of alkanes and cycloalkanes. Since the products from the Fischer-Tropsch synthesis will contain alkanes, alkenes, oxygenates, and some aromatics preliminary separations will be required. Initial work with C-14 labeled products will concentrate on lower boiling fractions, e.g.: *ca.* C_{12} or lower. Thus, the organic liquid fraction will be distilled to produce a lower boiling fraction. Liquid and/or dry chromatographic separations will be attempted to effect a separation, or partial separation , into compound classes. Other approaches to simplify the C-14 chromatogram will be attempted. One such scheme would be to brominate the alkenes so that a chromatogram could be obtained for a sample with olefins and for the same sample where the olefins have been brominated. The difference in C-14 traces would permit a more detailed C-14 distribution to be obtained.

The study will utilize basic promoters selected from Group IA and IIA, with emphasis on Group IA. Nonreducible oxide promoters will be selected on the basis of alcohol conversion selectivities. Our earlier work has shown alcohol dehydration selectivities as illustrated in figure I-30. Thus, oxides that are very selective for 1-alkene formation (ThO_2, ZrO_2) for cis 2 plus 1- alkene formation (Al_2O_3, Ga_2O_3) and unselective for alkene formation (HfO_2, ZnO) will be utilized for these studies.

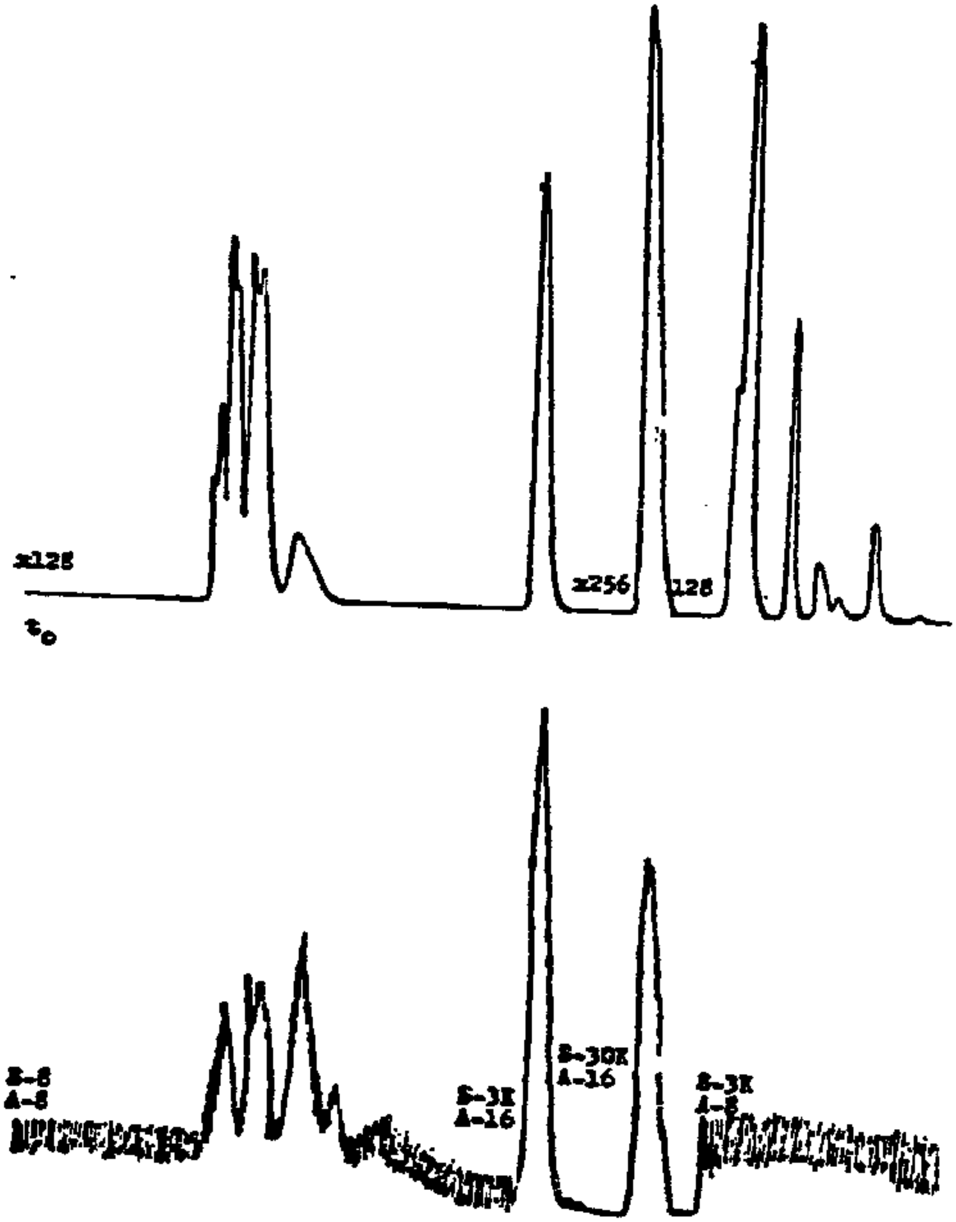


Figure I-29 Gas chromatograph (top) and radiochromatogram (bottom) of the products from the conversion of a naphtha containing C-14 labeled methylcyclohexane.

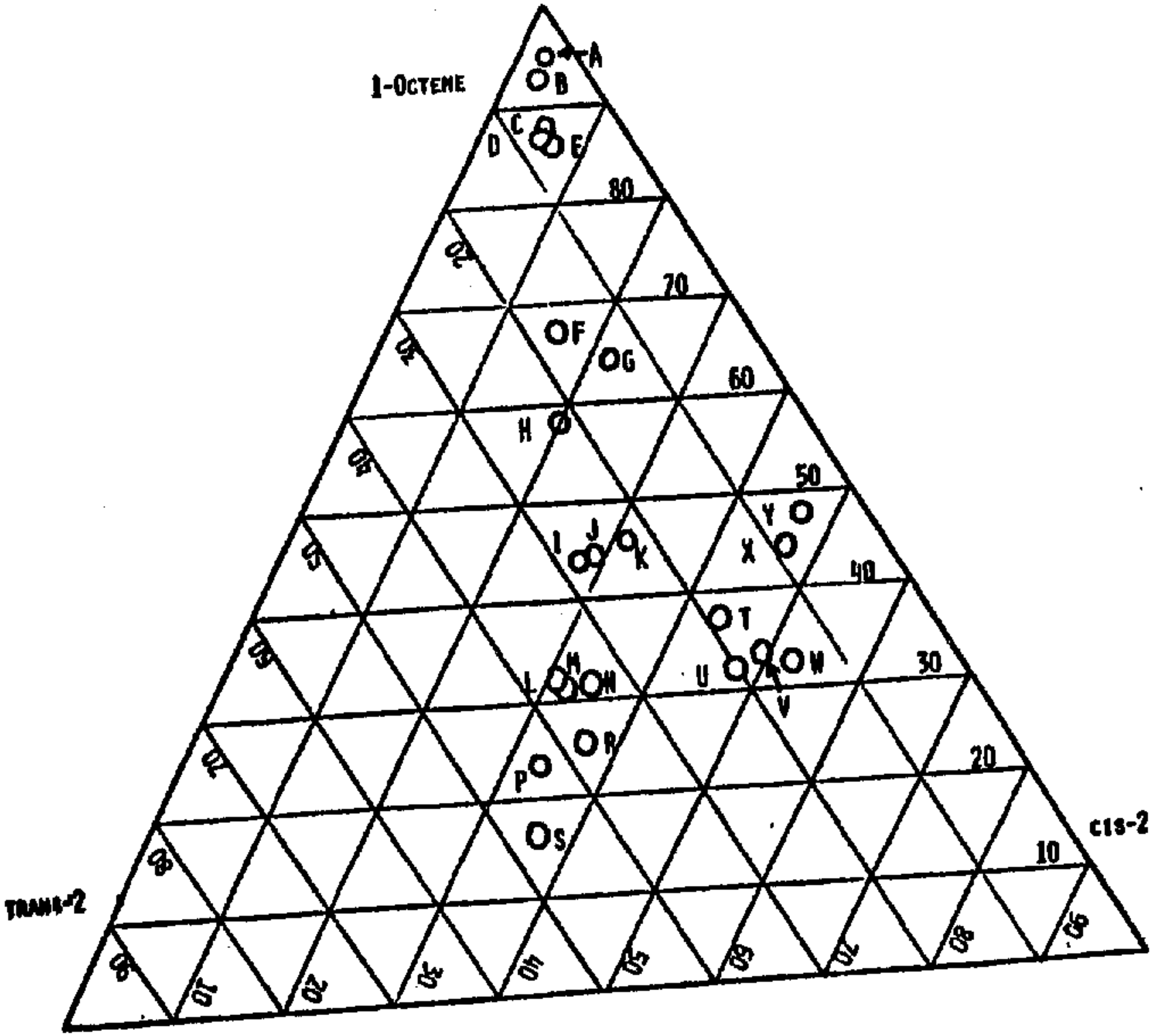


Figure I-30. Octene isomer distribution obtained from the conversion of 2-octanol with various metal oxide catalysts (the alkene distribution for the data representing the oxides labeled A through S is used to arrange the oxides in order of base strength.

REFERENCES

I-1. F. Fischer and H. Tropsch, Brennst. Chem., 4, 276 (1923).

I-2. H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses", John Wiley and Sons, New York, NY, 1951.

I-3. R. B. Anderson in "Catalysis" (P. H. Emmett, Ed.), Vol. 4, 257, Van Nostrand Reinhold, New York, NY (1956).

I-4. R. B. Anderson, "The Fischer-Tropsch Synthesis", Academic Press, Inc., New York, NY, 1984.

I-5. E. Jobling, "Catalysis and its Industrial Applications", J. and A. Churchill, London, 1961, pp. 10 and 43.

I-6. S. J. Thomson, J. Chem. Soc. Farad. Trans. I., 83, 1893 (1987).

I-7. M. E. Dry in "Catalysis", (J. Anderson and M. Boudart, Eds.), Springer-Verlag, Berlin, Vol. 1, Chapter 4, 1981.

I-8. B. Schliebs and J. Gaube, Ber. Bunsenges. Phys. Chem., 89, 68 (1985).

I-9. F. Fischer and H. Tropsch, Ges. Abhandl. Kenntnis Kohle, 10, 313 (1932).

I-10. J. T. Kummer, T. W. DeWitt and P. H. Emmett, J. Am. Chem. Soc., 70, 3632 (1948).

I-11. H. S. Taylor, Proc. Roy. Soc. (London), A108, 105 (1925).

I-12. J. T. Kummer and P. H. Emmett, J. Am. Chem. Soc., 73, 2886 (1951).

I-13. S. Z. Roginskii and O. Todes, Acta Physicochim. (USSR), 21, 519 (1946).

I-14. J. T. Kummer, H. H. Podgurski, W. B. Spencer and P. H. Emmett, J. Am. Chem. Soc., 73, 564 (1951).

I-15. J. T. Kummer and P. H. Emmett, J. Am. Chem. Soc., 75, 5177 (1953).

I-16. R. J. Kokes, W. K. Hall and P. H. Emmett, J. Am. Chem. Soc., 79, 2989 (1957).

I-17. R. J. Kokes, W. K. Hall and P. H. Emmett, ACS Div. Petroleum Chem. Preprints, Miami Meeting, April 7-12, 1957, p. 1271.

I-18. W. K. Hall, R. J. Kokes and P. H. Emmett, J. Am. Chem. Soc., 79, 2983 (1957).

I-19. W. K. Hall, R. J. Kokes and P. H. Emmett, J. Am. Chem. Soc., 82, 1027 (1960).

I-20. G. Blyholder and P. H. Emmett, J. Phys. Chem., 63, 962 (1959).

I-21. G. Blyholder and P. H. Emmett, J. Phys. Chem., 64, 470 (1960).

I-22. I. Toyoshima and P. H. Emmett, 19th National Meeting of the American Chemical Society, Chicago, IL, September 8-13, 1985.

I-23. V. Ponec in "Catalysis", (G. C. Bond and G. Webb, Eds.) The Royal Society of Chemistry, London, Vol. 5, pp. 48-89, 1982.

I-24. H. Pichler and H. Schulz, Chemie Ing. Techn., 48, 1162 (1970).

I-25. H. Schulz and H. D. Achtsnit, Revista portuguesa de Quimica. Lisboa, 19, 317 (1977).

I-26. H. Schulz, Erdol und Kohle-Erdgas-Petrochemie, 30, 123 (1977).

I-27. H. Pichler, H. Schulz and B. R. Rao, Liebigs Ann. Chem., 61, 719 (1968).

I-28. H. Schulz and H. D. Achtsnit, 5th Ibero-American Symp. on Catal., Lisbon, 1976.

I-29. H. Schulz and A. Zein el Deen, Fuel Processing Tech., 1, 45 (1977).

I-30. H. Schulz, B. R.Rao and M. Elstner, Erdol und Kohle, 23, 651 (1970).

I-31. H. Schulz, C_1 Mol. Chem., 1, 231 (1985).

I-32. H. Schulz, K. Beck and E. Erich, "Methane Conversion Symposium", (Bibby et al., eds.) Elsevier Sci. Pub., Amsterdam, 1987.

I-33. A.W. Fletcher and E.J. Gibson, Radioisotope Conf., 1954, Proc. of the Second Conf. Oxford 19-23 July, Vol. II, Phys. Sci. & Industrial Appl. (J.E. Johnson, Ed.) Butterworth Sci. Pub., London, 1954 p. 40.

I-34. S. Roginskii, Proc. of 1st UNESCO Congr., 1-16 (1958)(as reported by P.H. Emmett in ORNL lectures).

I-35. P. Biloen, J.N. Helle, G.G.A. van den Berg and W.M.H. Sachtler, J. Catal. 81 450 (1983).

I-36. J. Hapel "Isotopic Assessment of Heterogeneous Catalysis", Academic Press, New York, NY, 1958.

I-37. D.S. Jordan and A.T. Bell, J. Phys. Chem., 90, 4797, (1987); J catal, 108, 63.

I-38. C.A. Mims and L.E. McCandlish, J. Am. Chem. Soc., 107, 696 (1985).

I-39. C.A. Mims, L.E. McCandlish and M.T. Melchior in "Catalysis: Theory to Practice", (M.J. Phillips and M. Ternan, Ed.) Chem. Inst. Canada, Otttawa, Canada, Vol 4, p. 1992, 1988.

I-40. R.C. Brady III and R. Pettit, J. Am. Chem. Soc., 103, 1287 (1981).

I-41. F. Fischer and H. Tropsch, Brennst. Chem. 7, 97 (1926).

I-42. Brady, R.C., III; Pettit, R. H., J. Am. Chem. Soc., 102, 6181, (1980).

I-43. Masters, C. Adv. Organomet. Chem., 17, 61 (1979).

I-44. Henrici-Oliva, G.; Olive, S., Angew Chem., Int. Ed. Engl., 15, 136, (1976).

I-45. M.F. Zarochak, H.W. Pennline and R.R. Schehl, "An Experimental Reactor System for Investigation of Indirect Liquefaction Catalysts in Slurry Phase Operation". DOE/PETC/TR-84/5 (DE 84007876), February, 1984.

I-46. G.A. Huff, Jr., and C.N. Satterfield, Ind. Eng. Chem., Fundam, 21, 479 (1982); C.N. Satterfield and G.A. Huff, Jr., J. Catal., 73, 187, (1982); G.A. Huff, Jr., C.N. Satterfield and M.H. Wolf, Ind. Eng. Chem., 22, 258 (1983).