Catalysis Letters 7 (1990) 141–150

FISCHER-TROPSCH SYNTHESIS WITH AN IRON CATALYST: INCORPORATION OF ETHENE INTO HIGHER CARBON NUMBER ALKANES

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Fischer-Tropsch synthesis, iron catalyst, tracer studies, ^{14}C labeled ethene, alkenes, chain growth, radioactivity.

Tracer studies with ^{14}C labeled ethene show that for synthesis over a doubly promoted iron catalyst at 7 atm and ca. 60% CO conversion, higher carbon number products are formed from ethene initiation. About 10% of the added ethene (ethene/CO ~ 0.02) is incorporated into C_5^+ products and that ca. 85% of the ethene that is incorporated does so by initiating chain growth.

1. Introduction

The ability of alkenes to initiate and/or propagate chain growth in the Fischer-Tropsch synthesis has been of interest for many years. Emmett and coworkers, in their pioneering studies, indicated that only a few percent of ethene was incorporated [1] during their synthesis studies using an iron catalyst. Schulz et al. [2] found that about 10% of the ^{14}C labeled ethene added to a synthesis gas feed (consisting of 0.3 mole% alkene and $H_2/CO = 2.0$) was incorporated when they used an alkalized iron catalyst operated at 20 atm and 200 °C. A major fraction (> 50%) of the activity was in the C_3 and C_4 components; this result is expected for a mechanism that involved carbonylation of ethene rather than an Anderson-Schulz-Flory (ASF) polymerization mechanism. A more recent study [3] showed that the addition of ethene or propene markedly shifted the carbon number distribution to heavier products; here conditions were chosen so that the conversion was less than 1%. For this low conversion the products were methane and trace amounts of 1-alkanes.

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Snel and Espinoza [4] reported that co-feeding experiments with ethene or synthesis gas show that ethene readily initiates the synthesis without altering the chain growth probability. These latter workers reported that propagation by ethene was unlikely.

Recent results of Hanlon and Satterfield [5] as well as those of Arcuri et al. [6] emphasize the difficulty of deciding whether alkenes are incorporated into the complex Fischer-Tropsch product state. The alpha value defined by the Anderson-Schulz-Flory plot was not changed by the addition of alkenes; however, this is not very sensitive for a measure of incorporation.

We have converted a synthesis gas containing ^{14}C labeled ethene under conditions where 60–65% CO conversion occurred [7,8]. Using ^{14}C labeled ethene, the extent of incorporation of ethene can be measured directly. The products were separated to collect a fraction containing only alkanes. This alkane fraction was then further separated to permit a determination of the radioactivity for each carbon number n-alkane. The data indicate that the primary role of ethene is to initiate chain growth.

2. Experimental

The conversions were effected in a continuous stirred tank reactor (CSTR) at 260 ° C and 7 atm total pressure (medium pressure synthesis conditions). The feed gas consisted of $H_2/CO^* = 1.2$; each gas flow was monitored by mass flow regulators and was mixed prior to entering the 1 ℓ autoclave reactor. An United Catalyst Inc. C-73 doubly-promoted fused iron catalyst, was reduced in flowing H_2/CO for 72 hours at 400 ° C, passivated in a flow of 1% oxygen in nitrogen, transferred to the CSTR containing ca. 500 ml octacosane, and then re-reduced at 360 ° C in situ (details of the experimental procedures can be found in ref. [7]).

Ethene flow into the synthesis gas stream was controlled by its rate of synthesis from the catalytic dehydration of ^{14}C-ethanol at slightly greater than 7 atm pressure. The HZSM-5 catalyst operated at ca. 230 ° C, produced some 2 to 4% of ethane as well as lesser amounts of C_3, C_4 and traces of higher carbon number compounds. Several other common alcohol dehydration catalysts provided ethene with even more impurities when operated at 7 atm. and ca. 90% conversion. A dry ice trap to remove water, unconverted ethanol and diethylether was placed in-line between the reactor and the control valve used to feed ethene to the synthesis gas feed stream. Adjustment of the ethanol feed pump rate provided a constant flow rate of ethene so that the molar ratio ethene/CO was ca. 0.02.

The alkane fraction was separated from the other synthesis products using dry silica gel chromatography [7]. Then a high performance liquid chromatography (HPLC) [7] was utilized to separate the alkane fraction further to provide a pure sample of each carbon number. No single set of conditions could be found that would provide adequate separation of the entire C_{10}–C_{22} fraction; thus, the alkane fraction was subjected to three separation procedures, each using a solvent mixture selected to optimize separation for about 1/3 of the C_{10}–C_{22} carbon number range [9]. The ^{14}C in each HPLC fraction was determined using liquid scintillation techniques. Both GC and HPLC were utilized together with calibration curves to determine the molar concentration of each alkane eluting from the HPLC column and utilized for the ^{14}C counting measurements. Counting efficiencies depend upon instrument and scintillation solutions; thus, we obtained relative activities for sets of samples counted at one time. Thus, only trends, and not absolute CPM/μ mole, can be compared among data sets.

3. Results and discussion

The ^{14}C distribution in the synthesis products (including the activity in the unconverted ethene) shows that ethane contains 35–40% of the total ^{14}C, 1-propanol contains ca. 5–10% and the C_{5+} products contain ca. 10%. Ethene is unique among the alkenes since it undergoes extensive hydrogenation even in the presence of greater than 1 atm. partial pressure of unconverted CO [8]. Likewise, ethene undergoes carbonylation to produce labeled 1-propanol in disproportionate amounts relative to the higher carbon number normal alcohols that would follow an Anderson-Schulz-Flory distribution that includes 1-propanol [8].

The extent that ethene participates in chain initiation and chain growth with a promoted iron catalyst is of primary concern. Data for the radioactivity in the C_7–C_{16} alkanes are presented in fig. 1 together with curves that are anticipated for three chain growth scenarios that involve ethene in: (a) initiation only, (b) polymerization only, and (c) chain propagation (random incorporation into growing chains) with a lower probability of ethene incorporation than applies for polymerization.

Thus, schematically we have ($^*C_2$ represents radioactive ethene):

1. Initiation $^*C_2 + C_1 \rightarrow {}^*C_2\text{–}C\text{–}C\text{–}C \cdots C$
2. Polymerization $^*C_2 \rightarrow {}^*C_2\text{–}{}^*C_2\text{–}{}^*C_2 \cdots {}^*(C_2)$
3. Propagation $C_1 + {}^*C_2 \rightarrow C_1C_1{}^*C_2C_1 \cdots C_1 \cdots C_1{}^*C_2C_1 \cdots$
4. Initiation and Propagation
   $C_1 + {}^*C_2 \rightarrow {}^*C_2\text{–}C_1C_1 \cdots C_1 \cdots {}^*C_2C_1C_1C_1{}^*C_2 \cdots$

If ethene serves only as an initiator for chain growth, the radioactivity/mole for each alkane product will be equivalent, and a plot of radioactivity versus carbon number will be a straight line parallel to the X-axis as is illustrated in fig. 1. The experimental data are shown by the solid points; the general trend for the experimental data is essentially a logarithmic decrease in radioactivity/mole with increasing carbon number rather than the expected result for chain initiation.

In fig. 1 we have utilized the radioactivity that corresponds to an extrapolation of the line defined by the experimental data to carbon number 2 (●). If the radioactivity of this ethene is incorporated only by a polymerization reaction, the

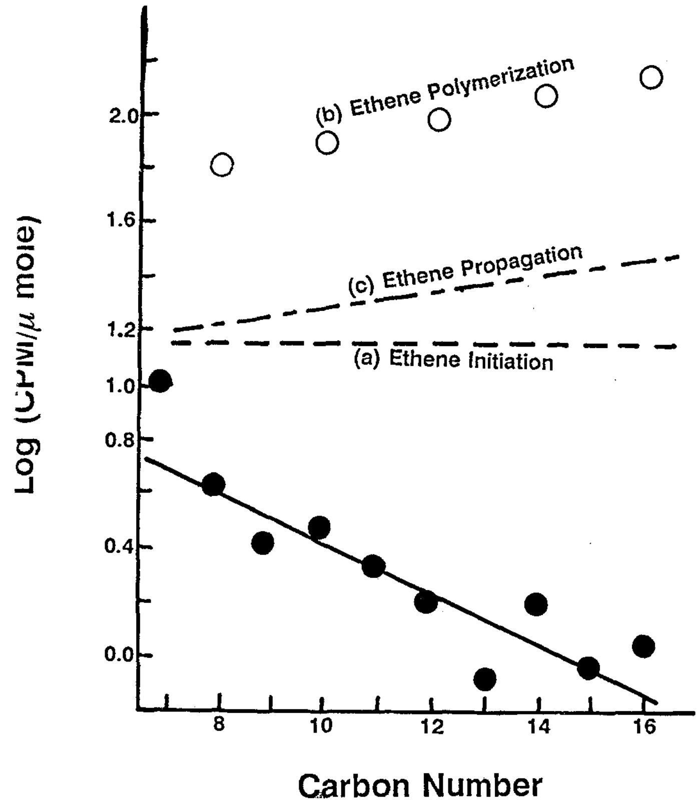

Fig. 1. The radioactivity of alkanes produced during synthesis with added ^{14}C labeled ethene versus carbon number (●). The broken lines indicate schematically for ethene initiation (— — —), ethene propagation (·–·–·) and ethene polymerization (o).

radioactivity will double for each increase of 2 in carbon number. This is also illustrated in fig. 1. The radioactivity versus carbon number plot for ethene polymerization will be a straight line and, if the radioactivity of ethene is assigned a value of 2, the line will have a slope of 1. On the logarithmic scale used in fig. 1, there will be curvature to the curve representing the hypothetical polymerization data; however, over the carbon range shown this is approximately a straight line with a positive slope.

Propagation by ethene is also possible. In this hypothetical scheme, ethene would add randomly to extend a growing chain by two carbon numbers. Polymerization may be viewed as propagation where the only chain growth occurs by ethene addition rather than the random addition of a C_1 species derived from CO and the C_2 species; in general, propagation by ethene will occur so that the probability of adding a C_1 species is greater than that of adding ethene. In all cases of propagation a plot of the radioactivity versus carbon number will produce a straight line with a positive slope between the limits of 0 and 1; the actual slope will reflect the relative contributions to chain growth by CO and ethene derived species. Thus, for the case where ethene does not initiate but only propagates chain growth, the hypothetical curve for propagation will extrapolate to zero activity for carbon number 2 and the line will be below the hypothetical line for the case of ethene serving only as a chain initiator. The schematic shown in fig. 1 that is labeled ethene propagation represents the case of ethene serving as both chain initiator and chain propagator.

It is clear that the experimental data are not consistent with any of the hypothetical radioactive patterns anticipated above. Instead, the radioactivity/mole decreases with increasing carbon number in the C_7–C_{16} range. This decrease in activity with carbon number is due to hold-up of products in the CSTR as well as to the normal CSTR kinetics for the delay of ^{14}C accumulation into the products of increasing carbon number.

A stirred-tank reactor was used in this study. ^{14}C labeled ethene was added, and products were collected, over a common 24 hour period. In a polymerization such as the Fischer-Tropsch reaction, attainment of steady-state ^{14}C label will require a longer time for each increase in carbon number product. Adjustment of the radioactivity data shown in fig. 1 to account for this accumulation has been done [10]; this correction will alter the slope of the experimental data line by nearly 25%. Hence, the correction for product accumulation only moves the experimental data toward the line defined by ethene initiation by a modest amount. In order to further adjust the experimental data to coincide with the line defined by initiation in fig. 1 a mechanism involving two independent chain growth pathways. Ethene initiates chain growth in one pathway with α corresponding to ca. 0.6 but ^{14}C labeled ethene does not build into the chain that corresponds to the chain growth pathway with α ca. 0.8 [10]. Using the alkane production data, the 25% adjustment for a CSTR, and the radioactivity of C_8 as a reference, the data point in fig. 1 will be adjusted to coincide with the hypothetical line for ethene serving as an initiator. With these two adjustments, the interpretation of the radioactvity/mole data for the C_7–C_{16} alkane fraction agrees with that obtained for the C_2–C_4 products when labeled alkene [8] or alcohol [7] is added to the syngas. The C_2–C_4 products produced during the addition of either ethene [8] or ethanol [7] show the anticipated line for radioactivity/mole that is parallel to the X-axis and are consistent with these compounds serving only to initiate chain growth.

The dilution of radioactivity/mole by the products of a second chain growth pathway is surprising. However, we have obtained this result repeatedly [7]. In fig. 2, our data obtained using a CSTR is compared with that reported by Schulz and coworkers [11] for data generated using a plug flow reactor. For this comparison the radioactivity of C_6 in both studies is taken as 100. The radioactivity appears to decrease linearly with alkane concentration for the data obtained using the plug-flow reactor while the decrease in radioactivity is logarithmically related to the carbon number for the products obtained using the CSTR. Even so,

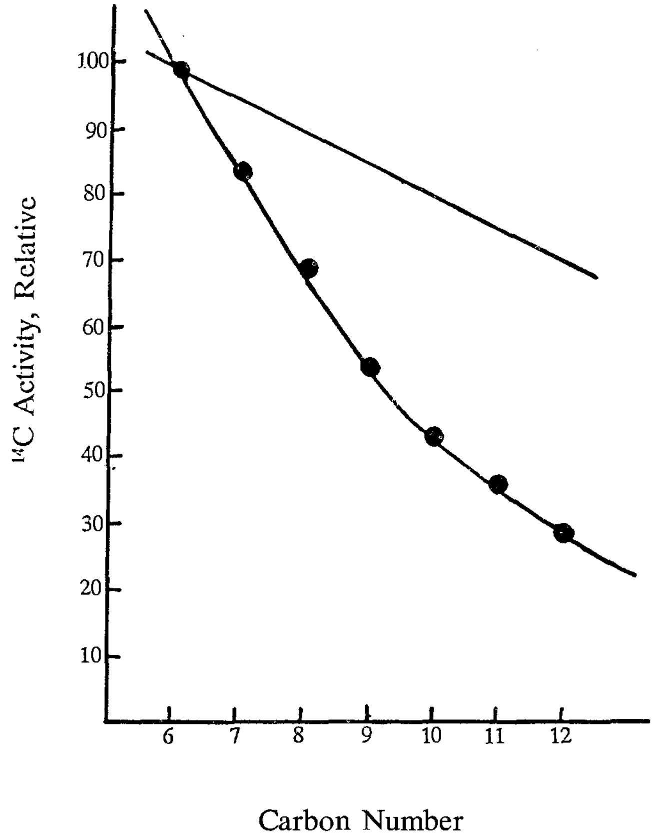

Fig. 2. Relative activity of alkanes from synthesis while adding ^{14}C labeled ethene using a flow reactor (solid line represents data from ref. [8]) and CSTR (———).

the results of the two studies are similar in that they show a radioactivity versus carbon number that does not fit any of the hypothetical growth mechanisms shown in fig. 1.

When the radioactivities for carbon number alkanes above C_{16} are considered, a different picture emerges (fig. 3). In the carbon number region C_{16}–C_{20} the radioactivity/mole increases with increasing carbon number. This is expected when ethene incorporates into the growing chain. The radioactivity of the added ethene was ca. 6,000 CPM/μmole while the activity of the C_{20} compound is only ca. 6.3 CPM/μmole. This means that only one of about 1,000 C_{20} molecules contains a ^{14}C from ethene. The radioactivity/mole increase represented by the C_{16}–C_{20} alkanes could also arise from chain initiation by ^{14}C labeled C_3–C_{15} alkenes produced by ^{14}C labeled ethene initiation. It is not possible to distinguish between ethene propagation and chain initiation by ^{14}C labeled higher carbon number alkenes. We have demonstrated that under similar reaction conditions C_5 and C_{10} alkenes do serve as chain initiators, although not as effectively as ethene [8]. Thus, it appears likely that a significant fraction of the increase in radioactiv-

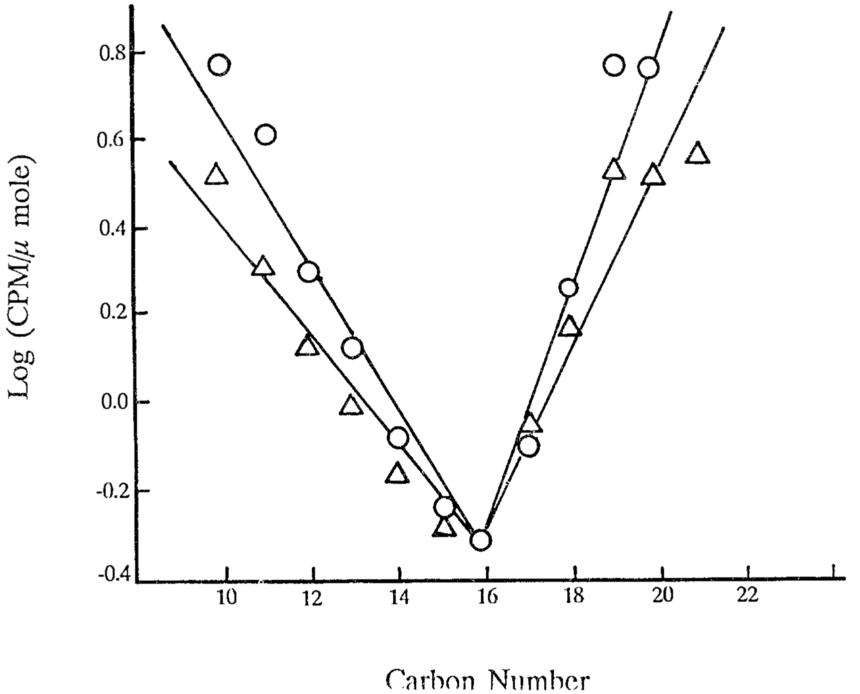

Fig. 3. The radioactivity of alkanes from carbon number 10 through 20 ((○) based on moles determined by gas chromatography; (△) moles determined by liquid chromatography).

ity/mole is the result of secondary reactions of the labeled lower carbon number alkenes.

We therefore consider the ^{14}C activity for any carbon number product to be derived from two sources: (1) chain initiation by ethene and (2) incorporation of ethene or chain initiation by higher carbon number alkenes. As can be seen in fig. 1, the activity/mole for chain initiation should be constant with carbon number; for this illustration we consider this activity to be f. The activity in products that result from random addition of ethene to a growing chain will fall on a line with a positive slope. The equation relating the activity introduced by a propagation mechanism and the carbon number is not simple for the system utilized. Thus we first consider the situation if the monomer, CO in the case of synthesis gas feed only, were labeled with ^{14}C. For a labeled C_1 monomer, the activity will increase by f each time that a carbon is added to a growing chain; hence the total activity of an alkane with n carbons will just be nf.

The radioactivity trend for the C_8–C_{16} products in fig. 1 is not consistent with the C_2–C_4 gaseous hydrocarbon products [8] generated at the same time. The C_2–C_4 data are consistent with ethene serving only as a chain initiator. In order to make the C_8–C_{16} alkane data lead to a conclusion that is consistent with the C_2–C_4 products, the radioactivities of the C_8–C_{16} alkanes have been corrected for (a) the kinetic factor that delays the attainment of steady state conditions for longer periods of time for each increasing carbonnumber compound, and (b) for two independent chain growth mechanisms, one that produces ^{14}C labeled products and one that does not.

The situation is more complicated when unlabeled C_1 monomer and labeled ethene are utilized since it is not possible to produce all labeled products in the random fashion as can be done with the labeled C_1 monomer. We assume that ethene, at least the C_2 entity, remains intact during the propagation; the absence of a detectable amount of radioactivity in methane provides a strong basis for this assumption. Since labeled C_3 can only form by the addition of labeled ethene to an unlabeled C_1 chain initiator, the activity of the C_3 products must be identical to that of the added ethene, f. Butane can be formed by three pathways: (1) initiation to produce butane with the same radioactivity as ethene, (2) propagation by addition of radioactive ethene to a C_2 chain, and (3) both initiation and propagation to produce butane with twice in the radioactivity of the ethene. Furthermore, the rates for initiation and propagation will be, in general, different. For lower carbon number products, the possible number of combinations of propagation by a C_2 unit requires that odd-even number alkane pairs (e.g. C_3 and C_4, C_5 and C_6) have the same radioactivity/mole. However, for the present considerations we are primarily interested in the order of magnitude comparisons.

For our purposes simplifications will be made by considering the addition of the C_2 unit. Ethene was synthesized from 1-^{14}C-ethanol so that ^{14}C doubly labeled ethene is not present. For ethene to have only a propagation role, the first C_2 unit must be unlabeled. Thus we can approximate the total radioactivity of an alkane with n carbons formed by propagation as $(n-2)/2f$. The radioactivity/mole for all alkanes formed by ethene propagation and chain growth by unlabeled C_1 units will be f.

For any carbon number alkane, the dilution factors discussed above must be the same for alkanes that result from initiation by ethene or from propagation by ethene. Thus, where the activity from initiation is equal to the activity from propagation (ca. C_{16} for the data in fig. 3) we have:

$$af = (1-a)[(n-2)/2]f$$

where f is the activity of ethene, n is the alkane carbon number, a is the fraction of the alkane C_n formed by initiation by ethene, af is the radioactivity of alkanes formed by ethene initiation and $(1-a)[(n-2)/2]f$ is the radioactivity of alkanes formed by ethene propagation. For $n = 16$ this leads to

$$a = (1-a)(16-2)/2$$

and $a = 7/8$. Thus only 1 of 8 ^{14}C containing alkane molecules result from propagation by ethene; ethene therefore serves predominately as a chain initiator. The fraction of ethene propagation will be decreased by the extent that secondary reactions of labeled C_3–C_{15} alkenes contribute to the radioactivity of C_{16}.

In conclusion, ^{14}C labeled ethene does incorporate into Fischer-Tropsch

Synthesis products produced with an iron catalyst using medium pressure synthesis conditions and ca. 60% CO conversion. The incorporation amounts to about 10% of the added ethene (moles ethene/moles CO = ca. 0.03 in feed) [7,8]. The dominant incorporation pathway for ethene is by chain initiation which accounts for more than 85% of the total incorporation.

Acknowledgment

This work was supported by the Commonwealth of Kentucky and the U.S. DOE through Contract. No. DE-AC22-84PC70029.

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