Chapter V

The Effect of Ethylene Addition on Fischer-Tropsch Synthesis

ABSTRACT

The C_2 products formed over Ru catalysts during Fischer-Tropsch synthesis often lie well below the Anderson-Schulz-Flory line describing the C_{4+} products. This has lead to speculation that either the surface precursor to these products plays a special role in chain growth, or that the ethylene formed re-adsorbs and re-enters the chain growth process. In this study, the effect of adding small amounts of ethylene to the CO/H_2 feed is investigated, using $^{13}CO/H_2$ and $^{12}C_2H_4$ to differentiate between the carbon sources. Ethylene addition suppresses methanation and results in an increase in the C_{3+} hydrocarbon formation rates. Isotopic tracer studies show that ethylene-derived carbon is present in the C_{3-8} product. Ethylene acts as an effective chain initiator, and ethylene-derived carbon accounts for 45% of a C_1 monomer species.

INTRODUCTION

The C_{3+} products observed during Fischer-Tropsch synthesis (FTS) are often characterized by an Anderson-Schulz-Flory (ASF) distribution. The concentration of methane usually lies above an extrapolation of the plot to lower carbon numbers, and the concentrations of C_2 and C_3 often lie below this line. The deviation of C_2 products from the ASF distributuion is particularly noticeable for FTS over Ru catalysts (1, 2). Two possible explanations have been proposed. The first is that the precursor to C_2 products may be characterized by a longer average lifetime than the precursors to higher molecular products (3, 4). The second possible explanation is that the ethylene, once formed, is readsorbed and reenters into the chain growth process (5, 6).

The first of these possibilities, the presence of a long lived C_2 intermediate during CO hydrogenation over Ru, has been suggested by Mims and co-workers (3, 4). Mims *et al.* (3) performed isotopic tracer experiments in which an abrupt switch was made from $^{12}CO/H_2$ to $^{13}CO/H_2$ in the reactor feed. NMR analysis of C_2 to C_5 olefin products allowed the determination of the fraction of ^{13}C at each position in these products. These studies showed that there are two distinct isotope replacement rates, with the two carbons at the aliphatic end having a distinctly longer average residence time than those in the remaining positions. Based on this evidence, the authors suggested the presence of two-carbon surface species that has a comparitively long residence time relative to higher molecular

weight surface species. The authors further proposed that these two-carbon species play the role of chain initiators. In a subsequent study, Mims et al. (4) proposed that these results could be explained by a model based on the assumption that initiators for chain growth spent over half their surface residence time as C_2 groups.

In situ addition of 1.2 % $C_2H_5NO_2$ to the CO/H_2 feed over a Ru/SiO_2 catalyst by Cavalcanti et al. (7) was performed to understand the role of the C_2 intermediate during FTS. The rate and selectivity for the C_3 through C_6 hydrocarbon products increased by 25% or more, while methane formation was reduced. An order of magnitude increase was seen in the C_2 and C_3 olefin to paraffin ratios. The addition of 1.2 % nitroethane did not alter the chain growth probability, which led the authors to speculate that the rates of chain initiation and propagation were both increased by comparable amounts when $C_2H_5NO_2$ was added. The authors concluded that both one-carbon and two-carbon units were formed, and that C_2H_x groups derived from $C_2H_5NO_2$ play an important role in enhancing chain initiation, while CH_x groups formed by hydrogenolysis participate in chain growth.

The effect of ethylene addition to CO/H_2 during FTS has been examined by a large number of investigators. Many of the older studies were conducted on Co and Fe catalysts and are reviewed by Eidus (8) and by Jordan and Bell (2). Over Co catalysts, added olefins readily incorporate into the FTS products and cause an increase in higher hydrocarbon production. Olefin readsorption is found to initiate hydrocarbon chains, the effectiveness of this process

decreasing rapidly with increasing chain length. Olefins also decompose to one-carbon fragments which then serve as monomer for chain growth. Over Fe catalysts, most researchers reported an increase in the production of higher molecular weight hydrocarbon products when olefins were added to the feed. Ethylene was also reported to act as a chain initiator.

Several recent studies of the effects of ethylene addition have been carried out over Fe and Co catalysts and these are briefly detailed here. Snel and Espinoza (9) have carried out ethylene addition experiments using an Fe catalyst. Their results indicated that the addition of 5 to 10 % ethylene to the feed readily initiates chain growth without altering the chain growth probability. The olefin selectivity increases, while the rate of hydrocarbon synthesis virtually doubles. A substantial fraction of the ethylene was incorporated into the C_3 products, whereas the amount of methane formed decreased. The authors also concluded that propagation by ethylene was unlikely. The incorporation of a small amount of ^{14}C-labelled ethylene during FTS over a doubly-promoted Fe catalyst was investigated by Tau et al. (10). 40% of the labelled ethylene was converted to ethane. The C_{5+} products contained $\approx$ 10% of the ethylene. With increasing carbon number, a decrease in radioactivity/mole was observed. The authors concluded that 85 % of the incorporated ethylene initiates chain growth.

Percy and Walter (11) used isotopic labelling and NMR spectroscopy to study the effects of adding 2 % ethylene to the synthesis feed passed over a Co/Al catalyst. From an analysis of the

propene, it was concluded that some ethylene dissociated to C_1 fragments. Ethylene incorporation as a C_2 unit was also observed. Adesina and co-workers (12) studied the effect of adding 1-2 % ethylene to different feed CO/H_2 mixtures over a commercial Co catalyst. The rates of formations of C_3-C_7 hydrocarbons increased from 50 to 100 %. The rate of methane formation and the probability of chain growth, α, remained unchanged. The effect of C_2H_4 addition was largest for the C_3 products, and decreased progressively for the higher hydrocarbons. The conclusion was that ethylene acted as a chain initiator.

In the case of FTS over Ru catalysts, it has been postulated that the low yields of C_2 and C_3 olefins may be due to the reincorporation of these products into growing chains (1). Studies by Kellner and Bell (1) showed that at concentrations above 1 %, ethylene addition enhanced the C_3 and C_4 product formation but suppressed the synthesis of C_{6+} hydrocarbons. Kobori et al. (13) have examined the effect of adding ^{12}C-labelled olefins to [13]CO/H_2 mixtures, using GC-MS product analysis. The addition of ethylene in a 1:1 ratio to the CO resulted in an increase in the C_3 and C_4 products, with C_3 showing the larger increase. The methanation rate decreased. Propylene addition caused an increase in the C_2 and C_4 product, with a concurrent drastic reduction in methane formation. Isotopic distributions for C_1, C_3-C_5 alkanes indicate extensive ^{12}C incorporation. When [12]C_2H_4 was added, 59 % of the methane was ^{12}C-labelled. More than 50 % of the C_3-C_5 alkanes consisted of only [12]C-

labelled molecules, whereas the percentage of products that were all ^{13}C-labelled was 4, 2 and 7 for C_3, C_4 and C_5 alkanes, respectively. ^{12}C-labelled propylene and octene addition also resulted in a large fraction of the C_1-C_5 alkanes containing ^{12}C. The authors concluded that carbon from the olefins can randomly incorporate into the reaction products. Morris et al. (14) studied the effects of ethylene and propylene addition on FTS over Ru supported on silica, 13x zeolite, titania and magnesia. For the silica and zeolite supported Ru, ethylene addition markedly enhanced the higher hydrocarbon formation rates without greatly influencing the mehanation rate, whereas for Ru/TiO_2 and Ru/MgO_2, the rate of higher hydrocarbons was enhanced by a factor of less than two and the methanation rate was reduced.

Jordan and Bell (2) have studied the interactions of ethylene with H_2 and CO over a Ru/SiO_2 catalyst, using isotopic labelling of the CO to differentiate carbon sources. These authors concluded that CO hydrogenation was strongly influenced by the presence of ethylene. The rates of C_3-C_6 hydrocarbon products increased, revealing maxima as the partial pressure of ethylene was increased. The methanation rate decreased when ethylene was added. With increasing partial pressure of ethylene, CO hydrogenation to hydrocarbons was progressively suppressed, while the hydroformylation of ethylene to propanal was enhanced. The product distribution could be described in terms of C_1 and C_2 monomer units that participate in chain propagation. The authors conclude that C_2H_4 is a more efficient source of intermediates for chain initiation

and chain growth than CO.

Mims and coworkers (15) have investigated the effects of adding ethylene, 1-hexene and 1-octene on FTS over Ru/ γ-Al$_2$O$_3$. Concentrations of upto 5 % ^{12}C- labelled olefin were added to H$_2$-^{13}CO mixtures. From an analysis of the products by GC-MS and NMR spectroscopy, it was established that alkenes could initiate the growth of higher molecular weight hydrocarbons, and with a lower probability, depolymerize to form lower molecular weight hydrocarbons. With added alkene concentrations of less than 1 %, the product distribution was substantially altered. The production of all hydrocarbon products except methane was increased. The increase in rates was highest for carbon numbers adjacent to the added alkene, and decreased for progressively higher and lower carbon numbers. NMR analysis of the products showed the presence of a C$_2$ initiator at the alkyl end of the 1-alkene products when ethylene was co-fed. The fractional ^{12}C-labelling of the last two positions of the 1-alkenes was $\approx$ 75%. These results were attributed to chain initiation from adsorbed ethylene and further growth from a common C$_1$ pool. About 54 % of the carbon in the methane formed when ethylene was added to the feed derived from the ethylene.

The objective of this study was to investigate the effect of adding small amounts of ethylene to the CO/H$_2$ feed mixture, using labelled ^{13}CO and ^{12}C$_2$H$_4$ in order to differentiate between the carbon sources. Of particular interest was the determination of the extent to which chain initiation and propagation are affected by the added

ethylene.

EXPERIMENTAL

A 3.3% Ru/TiO_2 (Degussa P25) catalyst was used. Catalyst preparation and characterization have been described in Chapter 4. 1.35 gm of catalyst was loaded into a quartz microreactor. The product sampling and analysis system used were also identical to that described in Chapter 4.

Addition of ethylene to the feed were accomplished by using mixtures of 420 ppm ethylene in He (Matheson Gas) or 2 % ethylene in He (Matheson Gas). All experiments were conducted at 1 atm, 463 K and a H_2/CO ratio of 3. Total flow rate to the reactor was 100 cm3/min comprised of 30 cm3/min of H_2, 10 cm3/min of CO and He or (He+ethylene) making up the remaining 60 cm3/min.

RESULTS

After 20 min of reaction in 10:30:60 mixture of $CO:H_2:He$, the He in the feed was abruptly replaced by a He/420 ppm ethylene mixture. This resulted in the effective addition of 252 ppm of ethylene to the reactor feed. This concentration is similar to the amount predicted for C_2 by an ASF line based on the C_{4+} products. This small amount of ethylene caused almost no change in the rate of hydrocarbon production, as seen in Figure 1. There was also no
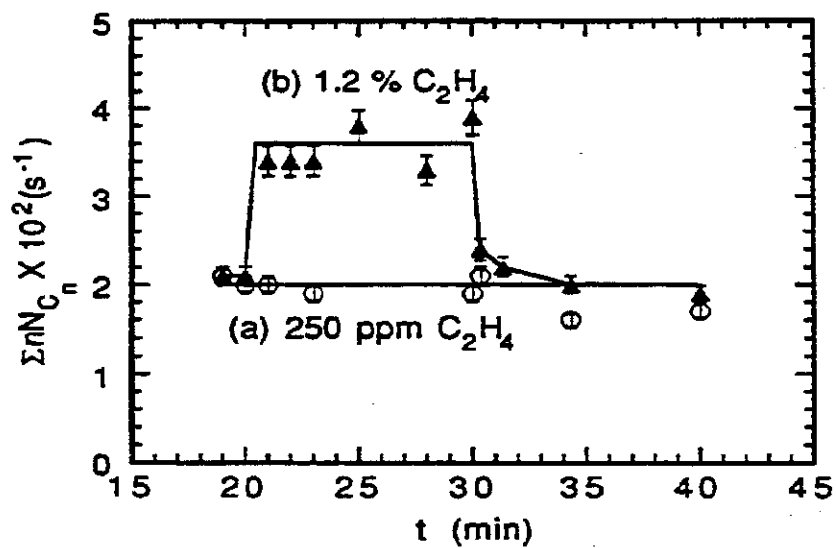
Fig. 1. Effect on total carbon in hydrocarbon product when ethylene is added to the CO/H_2 feed; (a) 250 ppm C_2H_4. (b) 1.2 % C_2H_4. Reaction conditions: T= 463 K; $H_2/CO = 3$. Ethylene is added from t = 20 min to t = 30 min.

change in the chain growth probability, α, which remained at 0.80 ± .02. Product analysis indicates that the C_2 product rose by a level equal to 32 % of the added ethylene. 68% of the added ethylene incorporated into products other than ethane, accounting for 2 % of these products. The rates of formation of the C_1 and C_{3+} products were unchanged. When 1.2 % ethylene was similarly introduced after 20 min of reaction, an immediate effect was seen (Fig. 1). The total rate of hydrocarbon production rose by a factor of 1.5. This rate is calculated as ΣnN_{Cn}, where N_{Cn} is the turnover frequency of the total hydrocarbon product of carbon number n. Figure 2 shows that the addition of 1.2 % C_2H_4 caused a small decrease in α to of 0.75 ± 0.2. After 30 min, a switch was made in the He stream back to pure He, and the activity dropped to the initial level in $CO/H_2/He$ and α rose to 0.8. Some deactivation was seen after 40 min on-stream consistent with the deactivation rate estimated for this catalyst in Chapter 2.

Experiments were also conducted in which reaction was started up in $CO/H_2/He/1.2$ % C_2H_4 and samples were taken between 20 and 40 min of reaction; these were then compared with reaction in the absence of ethylene. The results obtained confirmed the activity and α changes observed in the step change experiments shown in Fig. 1.

Of the ethylene fed, 12 % was converted to ethane and 82 % to other products. From these figures, it is determined that 68 % of the total hydrocarbon product, exclusive of C_2 products, derives from C_2H_4. The addition of 1.2 % C_2H_4 to the feed caused the CO
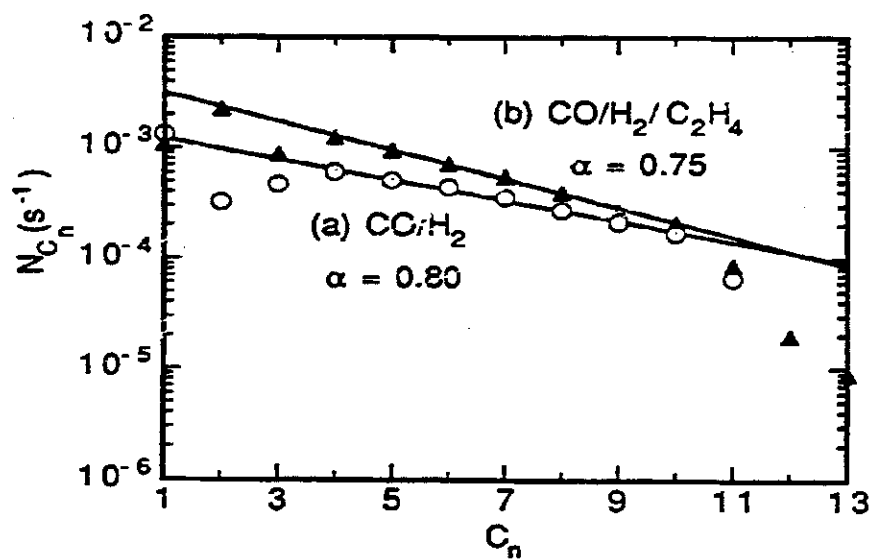
Fig. 2. Anderson-Schulz-Flory plot of N_{Cn} versus carbon number, C_n, in a) CO/H_2; (b) $CO/H_2/C_2H_4$. Reaction conditions: T= 463 K; H_2/CO = 3.

conversion to decrease from 20 % to 9 %.

The methanation rate decreased by 30 % upon C_2H_4 addition. Activity increases were observed for other products also, as can be seen from Figs. 2 and 3. Ethylene addition also resulted in an increase in the olefin content of the products. Figure 4 shows the olefin/paraffin ratio in the absence and presence of ethylene. There was no change in the identity of the reaction products formed when ethylene was added to the feed.

Experiments were also conducted in which 1.4 % C_2H_4 was reacted with 30 % H_2 in the absence of CO. The ethylene was completely converted since no ethylene was detected by gas chromatographic analysis of the reactor effluent. 54% of the ethylene was converted to methane, 43 % to ethane and 3 % to higher hydrocarbons upto C_{14}, which were detected in trace amounts.

To determine the extent to which the carbon derived from ethylene enters into the formation of hydrocarbon products, isotopic labelling was used. Reaction was initiated in [12]CO/H_2/He/1.2 % C_2H_4 and after 20 min, the CO in the feed was replaced by [13]CO. After 10 min in labelled CO, the CO in the feed was switched back to [12]CO. Isotope-ratio gas chromatography (16, 17, 2) was used to study the incorporation of the ^{13}C from the CO into the hydrocarbon products from C_3-C_8. In order to assess the effect of the added ethylene, this experiment was repeated in the absence of ethylene in the He diluent stream.

Figure 5a shows the the transient response of the fraction of each product that is [13]C- labelled, F_n (n=3-8), when the feed is
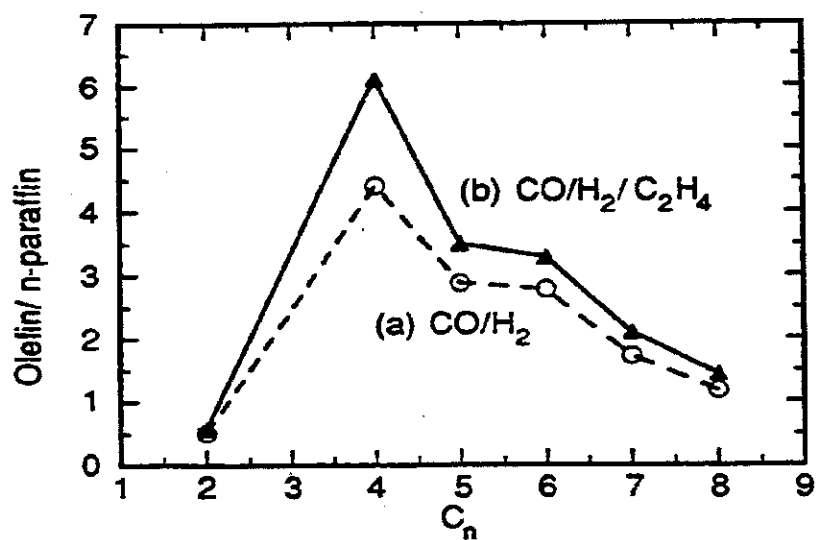
Fig. 4.   Olefin/n-paraffin ratio as a function of carbon number, C_n in (a) CO/H_2; (b) $CO/H_2/C_2H_4$. Reaction conditions: T= 463 K; H_2/CO = 3.

changed from $^{12}CO/H_2/He$ to $^{13}CO/H_2/He$. These traces are similar to those presented in Chapter 4 and are representative of a sequential incorporation of ^{13}C into the products. Figure 5b shows the corresponding transient responses when 1.2% ethylene is present in the feed. Due to the presence of the $^{12}C_2H_4$, the products are never completely ^{13}C labelled, and consequently, the steady-state value of the ^{13}C fraction after 10 min in $^{13}CO/H_2/He/^{12}C_2H_4$ is used to normalize the fractions.

Table 1 lists the fraction of ^{12}C-labelled carbon in the C_3-C_7 products at steady-state reaction in $^{13}CO/H_2/He/^{12}C_2H_4$ (i.e., after 10 min of reaction). ^{12}C-labelled ethylene and ethane were also detected. These products were virtually 100% ^{12}C labelled because of the high concentrations of $^{12}C_2H_4$ in the feed.

DISCUSSION

Ethylene added to the CO/H_2 feed can facilely incorporate into the chain growth process; 68 % of the ethylene was incorporated into the non-C_2 hydrocarbon product when 250 ppm of ethylene was added to the CO/H_2 feed, and 82 % of the added ethylene was incorporated into C_1 and C_{3+} products when 1.2% ethylene was added. At the lower concentration, ethylene does not affect the rates of C_1 and C_{3+} product formation, but only displaces 2 % of the ^{13}CO. At a level of 1.2 % C_2H_4, the overall rate of hydrocarbon product formation rose by 50 % (Fig. 1). This increase is similar to that
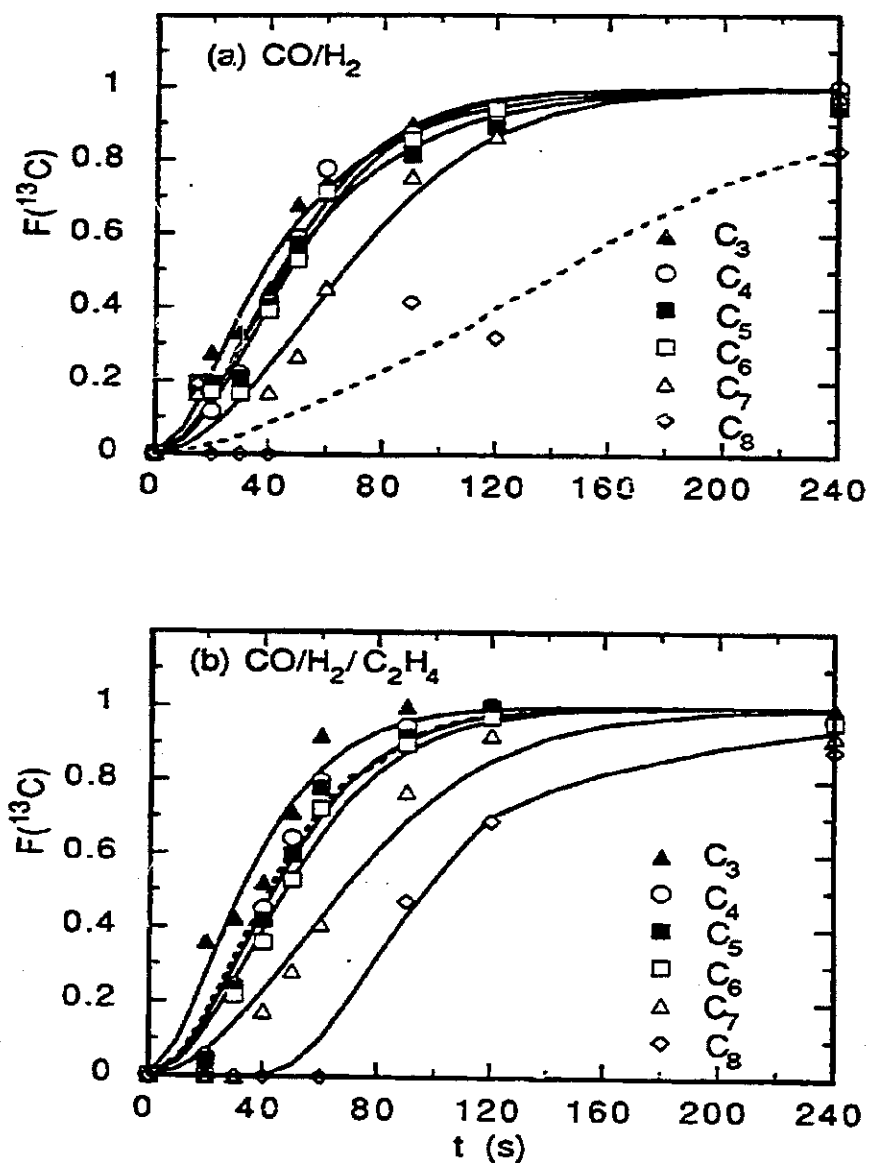
Fig. 5. $F(^{13}C)$ rise in the C_3-C_8 products; transient response after (a) a switch from $^{12}CO/H_2$ to $^{13}CO/H_2$ at t = 0; (b) a switch from $^{12}CO/H_2/^{12}C_2H_4$ to $^{13}CO/H_2/^{12}C_2H_4$ at t = 0. Reaction conditions: T= 463 K; $H_2/CO = 3$.

TABLE 1

Fraction ^{12}C in product at steady state in a
1.2 % $^{12}C_2H_4$/10 % ^{13}CO/30 % H_2/He mixture

Carbon Number	F^{12}C (expt)	F^{12}C (C$_2$ initiator)	F^{12}C (C$_2$ initiator + 0.45 $^{12}C_1$)
3	0.79	0.66	0.82
4	0.77	0.50	0.73
5	0.68	0.40	0.67
6	0.65	0.33	0.63
7	0.64	0.29	0.61
8	0.57	0.25	0.53

observed by other researchers upon ethylene addition (1, 2, 8, 9, 12-15). Conversion of CO to products is reduced from 20 % to 9 % in the presence of 1.2% ethylene (i.e., ethylene displaces 55 % of the ^{13}CO) in a manner similar to that observed by Jordan and Bell (2), and CO accounts for only 32 % of the hydrocarbon product. The α value fell slightly on ethylene addition, (Fig. 2), in contrast to other reports (2, 9, 15). As can be seen from Figs. 2 and 3, this is due to the activity increase on ethylene addition being most pronounced for the C_3 and C_4 products and progressively decreasing for longer chains. This progressive decline in enhancement for the higher hydrocarbons was also noted by Mims et al. (15) .

An increase in olefin to paraffin ratio (shown in Fig. 4) on 1.2 % C_2H_4 addition is also in agreement with observations made by Snel and Espinoza (9). A concurrent decrease in methanation is seen here and has also been reported by other researchers (2, 9, 13-15). A probable cause is a lower hydrogen coverage on the surface that results in a reduced hydrogenation capability of the catalyst in the presence of ethylene, which would account for both these changes in product selectivity.

The isotopic transients presented in Fig. 5 show that the dynamics of ^{13}C incorporation into the products is not altered by the presence of ethylene. This indicates that the added ethylene does not alter the mechanism of chain propagation and termination.

The results shown in Table 1 indicate that in the presence of 1.2% C_2H_4, a large fraction of the products are ^{12}C-labelled. If the added ethylene only contributes $^{12}C_1$ units to the monomer pool, the

fraction of ^{12}C in all the products should be the same, at a level that reflects the fraction in this pool. The progressive decrease in the fraction of ^{12}C carbon suggests that adsorbed ethylene acts primarily as a chain initiator. If this were the only role of the added $^{12}C_2H_4$, then the fraction of ^{12}C would be 66 % in the C_3 products and the ^{12}C fraction would decrease rapidly in the higher molecular weight products with increasing number of carbon atoms. Table 1 shows the results of this calculation. Comparison with the experimental results reveals that the observed fractions are higher than these estimates and decrease much more gradually.

A slower decrease in the fraction of ^{12}C-labelled products would occur, if, in addition to acting as a chain initiator, $^{12}C_2H_4$ contributes to the pool of C_1 monomer units (e. g., $CH_{2,s}$). It can be assumed that a fraction of the C_1 monomer pool is ^{12}C-labelled, f_m, and further, that there is a constant fraction of C_2 initiators in the C_{3+} products, f_i. This would lead to the overall fraction of ^{12}C in a product of carbon number n, $\bar{F}_n(^{12}C)$ to be:

$$F_n(^{12}C) = \frac{1}{n} [2f_i + (n-2)f_m]$$

A multiple-regression of this equation in two variables over the data for F_n (n = 3-8) yields values of f_i = 1.03 and f_m = 0.45. This indicates that the experimental results are consistent with every product molecule containing a $^{12}C_2$ initiator unit, and furthermore, that 45 % of the monomer is ^{12}C-labelled. Fixing this as the isotopic composition of the monomer pool, one can calculate the isotopic composition of the C_3-C_8 products. The results shown in Table 1

indicate that the calculated isotopic compositions agree reasonably well with those observed.

The results in Table 1 can be compared with those of Kobori *et al.* (13) and Mims *et al.* (15). Kobori and co-workers (13) report that when $^{12}C_2H_4$ was added to $^{13}CO/H_2$ at a level of 0.79:1:2, 59 % of the methane was ^{12}C-labelled. $^{13}C_i$ fractions (fraction of molecules containing i ^{13}C atoms) are reported for C_3-C_5 alkanes. These data show that 81 % or more of the C_{3-5} molecules contain a $^{12}C_2$ unit. Calculations from Kobori *et al.*'s data show that the total fraction of ^{12}C-labelled carbon is 85 % in the C_3 product, 88 % in the C_4 product and 69 % in the C_5 product. These data are also consistent with a model assuming extensive $^{12}C_2$ initiation and a monomer pool that contains 50-60 % ^{12}C. The 59 % fraction of this pool that is indicated by the isotopic composition of the methane is probably higher than that of 45 % indicated by our study due to the higher ratio of ethylene to CO used here. Mims *et al.* (15) report that when less than 5 % ethylene was added to the CO/H_2 feed, the methane contained $\approx$ 55 % ^{12}C, and that the fractional ^{12}C-labelling of the last two positions in the C_3 and C_4 1-olefins was 75%. These results can be compared to ʼʼe 45 % ^{12}C-labelled monomer pool, and the 100 % $^{12}C_2$ initiation estimated here.

Jordan and Bell (2) have proposed that C_2 species can participate in chain propagation. If C_2 species were more efficient chain propagation units than C_1 species, the products with an even number of carbon units would probably contain more ^{12}C than the adjacent odd number products. Also, the incorporation of the ^{13}C

from CO would be slower in the even number products. The data presented in Table 1 indicates that the fraction of ^{12}C falls off with increasing carbon number, and the data shown in Fig. 5 show that ^{13}C incorporates successively into each carbon number product from C_3 upwards. This leads to the conclusion that C_2 species are not more effective chain propagation units that C_1 species.

The data in Fig. 3 indicate that the maximum activity increase is seen for the C_4 product, in contrast to the results of Adesina *et al.* (12) and Mims *et al.* (15) who reported a maximum increase in the C_3 product. Data by Jordan and Bell (2) indicate that the rate of production of the C_4 hydrocarbons can exceed that of the C_3 hydrocarbons for a range of reaction conditions used. Also, C_4 is the dominant product when ethylene is present in the feed (see Fig. 2), as has also been noted by Jordan and Bell (2). This could be due in part to ethylene homologation; calculations based on the observed isotopic composition, a $^{12}C_2$ initiator, a 45 % ^{12}C monomer pool and allowing for homologation indicate that roughly a fifth of the C_4 product may be formed by this process.

CONCLUSIONS

The effect of adding small amounts of ethylene to the CO/H_2 feed show that ethylene addition results in a substantial rate increase in hydrocarbon production, with the exception of methane. At an ethylene/CO ratio of 0.12, the ethylene accounts for 68 % of the hydrocarbon product. Isotopic tracer studies show that the

ethylene-derived carbon is present in the C_3-C_8 product, the fraction of such carbon decreasing as the hydrocarbon chain length increases. These observations lead to the conclusion that ethylene acts as an effective chain initiator, and as a source of carbon for C_1 monomer units. For the conditions of the present experiment, 100 % of the chain initiator and 45 % of C_1 species for chain propagation are derived from ethylene.

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