Catalysis Letters 14 (1992) 305–313

The role of C_2 intermediates in Fischer–Tropsch synthesis over ruthenium

Kamala R. Krishna and Alexis T. Bell

Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, CA 94720-9989, USA

Received 3 March 1992; accepted 1 May 1992

The C_2 products formed over Ru during Fischer–Tropsch synthesis often lie well below the Anderson–Schulz–Flory line describing the C_{4+} products. This has led to speculation that either the surface precursor to C_2 hydrocarbons is exceptionally long lived, or that the ethylene formed by CO hydrogenation readsorbs and thereby reenters the chain growth process. In this study, the role of ethylene readsorption on the dynamics of chain initiation and growth is investigated using $^{13}CO/H_2$ and $^{12}C_2H_4$ to differentiate between the carbon sources. Ethylene addition is found to suppress the rate of methanation and increase the rates of formation of C_{3+} hydrocarbons. Ethylene serves as an effective chain initiator, as well as a source of C_1 monomer species which participate in chain propagation. No evidence is seen, though, for the participation of C_2 species in chain propagation.

Keywords: C_2 intermediates; Fischer–Tropsch synthesis

1. Introduction

The C_{4+} products observed during Fischer–Tropsch synthesis (FTS) are often characterized by an Anderson–Schulz–Flory (ASF) distribution. The concentration of methane sometimes 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 [1]. The deviation of C_2 products from the ASF distribution is particularly noticeable for FTS over Ru catalysts [2,3]. 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 [4,5], and the second is that ethylene, once formed, is readsorbed and reenters the chain growth process [6,7].

The presence of a long-lived C_2 intermediate during the hydrogenation of CO over Ru, has been suggested by Mims and co-workers [4,5]. NMR analysis of the C_2 through C_5 olefins produced following an abrupt switch in the feed from

$^{12}CO/H_2$ to $^{13}CO/H_2$ was used to determine the fraction of ^{13}C at each position in the hydrocarbon chain. These studies showed that the first two carbons at the aliphatic end have a distinctly longer average residence time than the carbon atoms in the remaining positions. Based on this evidence, the authors suggested the presence of C_2 surface species that act as chain initiators and have a comparatively long residence time relative to higher molecular weight adspecies.

Additional evidence for the special role of C_2 intermediates has been reported by Cavalcanti et al. [8], who investigated the effects of adding $C_2H_5NO_2$ to a mixture of H_2 and CO passed over a Ru/SiO_2 catalyst. Addition of 1.2% $C_2H_5NO_2$ increased the rate of formation of C_3 through C_6 hydrocarbons by 25% or more, while the rate of methane formation decreased, and an order of magnitude increase occurred in the C_2 and C_3 olefin to paraffin ratios. The addition of $C_2H_5NO_2$ had no effect, though, on the chain growth probability. It was concluded that both one-carbon and two-carbon units are formed from $C_2H_5NO_2$, and that the C_2 species play an important role in enhancing chain initiation, while the C_1 species formed, by hydrogenolysis, participate in chain growth.

The readsorption of ethylene during FTS over Ru catalysts has been examined by a number of investigators. Kellner and Bell [2] have shown that at concentrations above 1%, ethylene addition to a 3/1 mixture of H_2 and CO enhances the formation of C_3 and C_4 products, but suppresses the formation of C_{6+} products. Similar results have been reported by Kobori et al. [9]. Using $^{12}C_2H_4$ and ^{13}CO in a 1:1 ratio, these authors found that 59% of the CH_4 was ^{12}C-labeled and more than 50% of the C_3–C_5 alkanes consisted of only ^{12}C-labeled molecules. The percentages of C_3, C_4, and C_5 products that were all ^{13}C-labeled were 4, 2, and 7%, respectively. While Kobori et al. [9] did not carry out a detailed analysis of the isotopic distribution of carbon atoms in each product, they concluded that carbon atoms from the added olefin can incorporate randomly into the products. The effects of C_2H_4 concentration on FTS over Ru have been investigated by Jordan and Bell [10]. They found that as the concentration of $^{12}C_2H_4$ increased relative to that of ^{13}CO, the conversion of CO to hydrocarbons decreased and the conversion of C_2H_4 to C_1 and C_{3+} hydrocarbons increased. Based on the distribution of products observed at C_2H_4/CO ratios above unity, it was concluded that C_1 and C_2 units derived from C_2H_4 can participate in chain initiation and growth, together with C_1 units derived from CO. A more detailed analysis of the products formed by adding $^{12}C_2H_4$ to a $^{13}CO/H_2$ mixture has been reported recently by Mims et al. [11]. ^{13}C-NMR analysis of the products revealed that the last two carbon atoms of C_3 and C_4 1-olefins were 75% ^{12}C-labeled, whereas the remaining carbon atoms were about 52% ^{12}C-labeled. These results were attributed to preferential chain initiation by a C_2 species derived from C_2H_4 and subsequent chain growth by C_1 species derived from C_2H_4 and CO.

The objective of this study is to investigate the effects of adding small amounts of C_2H_4 on the elementary processes occurring during FTS over Ru. ^{13}CO and $^{12}C_2H_4$ were used to differentiate the sources of carbon. Of particular interest was a determination of the extent to which the added ethylene affects the dynamics of chain initiation and growth, as well as the relative concentration of C_1 and C_2 species on the catalyst surface.

2. Experimental

A 3.3% Ru/TiO_2 (Degussa P25) catalyst was used. The preparation and characterization of this catalyst are described in ref. [12]. 1.35 g of catalyst was loaded into a quartz microreactor and reduced in flowing H_2 at 503 K for 2 h. The distribution of reaction products was determined by gas chromatography, and the isotopic distribution of ^{12}C and ^{13}C was determined using a specially designed gas chromatography/mass spectrometer system [10,12].

Addition of ethylene to the feed was 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 cm^3/min comprised of 30 cm^3/min of H_2, 10 cm^3/min of CO and He or a He/C_2H_4 mixture making up the remaining 60 cm^3/min.

3. Results

The effects of ethylene addition on the steady-state activity and product distribution were investigated in the following manner. After 20 min of reaction in an $H_2/CO/He$ mixture, the stream containing pure He was switched to one

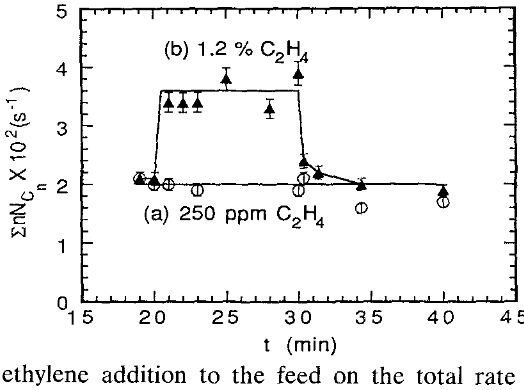

Fig. 1. The effect of ethylene addition to the feed on the total rate of carbon conversion to hydrocarbon products: (a) 250 ppm C_2H_4; (b) 1.2% C_2H_4. Reaction conditions: $T = 463$ K; $H_2/CO = 3$. Ethylene is added from $t = 20$ min to $t = 30$ min.

Table 1
Effects of C_2H_4 addition on the distribution of products derived from C_2H_4 and the conversion of CO. Reaction conditions: $T = 463$ K; $P = 1$ atm; $H_2/CO = 3$; $Q = 100$ cm^3/min. The CO conversion in the absence of C_2H_4 addition is 20%

$[C_2H_4]$ (ppm)	% C_2H_4 to non-C_2 products	% of HC (non-C_2) products due to C_2H_4	% C_2H_4 to C_{3+} products	Decrease in CO conversion (%)
250	68	2	–	2
12000	82	68	80	11

containing a C_2H_4/He mixture. Fig. 1 shows that the addition of 250 ppm of C_2H_4 to the synthesis gas has virtually no effect on the overall rate of hydrocarbon production, whereas the addition of 1.2% C_2H_4 increases the overall rate of hydrocarbon production by 50%. At the level of 252 ppm, C_2H_4 addition has no effect on the probability of chain growth, α, which remains at 0.8. Raising the concentration of C_2H_4 to 1.2% decreases the value of α to 0.75.

The effects of feed composition on the conversion of CO and C_2H_4 are presented in table 1. In the absence of ethylene addition, the conversion of CO is 20%. When 250 ppm of C_2H_4 is added to the feed, the CO conversion decreases to 18%. The conversion of C_2H_4 to C_1 and C_{3+} products is 68%, which corresponds to 2% of these products. Increasing the C_2H_4 concentration in the feed to 1.2% causes a decrease in the CO conversion to 9%. The conversion of C_2H_4 to C_1 and C_{3+} products in this case is 82%, which corresponds to 68% of these products being derived from C_2H_4. Table 1 shows further that 12% of the C_2H_4 is converted to ethane and 80% to C_{3+} products. Therefore, very little of the C_2H_4 undergoes hydrogenolysis to CH_4. For comparison, results are also presented for the reaction of 1.4% C_2H_4 and H_2. In this case, 57% of the C_2H_4 is converted to C_1 and C_{3+} products, most of which is CH_4.

Isotopic labeling experiments were carried out to determine the extent to which the carbon derived from ethylene enters into the formation of hydrocarbon products. Reaction was initiated by passing a $^{12}CO/H_2/He$ mixture containing 1.2% $^{12}C_2H_4$ over the catalyst. After 20 min, the ^{12}CO in the feed was replaced by ^{13}CO, and after an additional 10 min, the ^{13}CO in the feed was switched back to ^{12}CO. Isotopic-ratio gas chromatography/mass spectrometry was used to determine the dynamics of ^{13}C incorporation into the C_3–C_8 hydrocarbons. To assess the effect of the added ethylene, this experiment was repeated without the addition of ethylene to the He diluent stream.

Fig. 2a shows the transient response of the fraction of each product that is ^{13}C-labeled, $F_n(t)$ ($n = 3$–8), when the feed is switched from $^{12}CO/H_2/He$ to $^{13}CO/H_2/He$. The observed transient responses are similar to those reported in ref. [12], and are representative of a sequential incorporation of ^{13}C into the

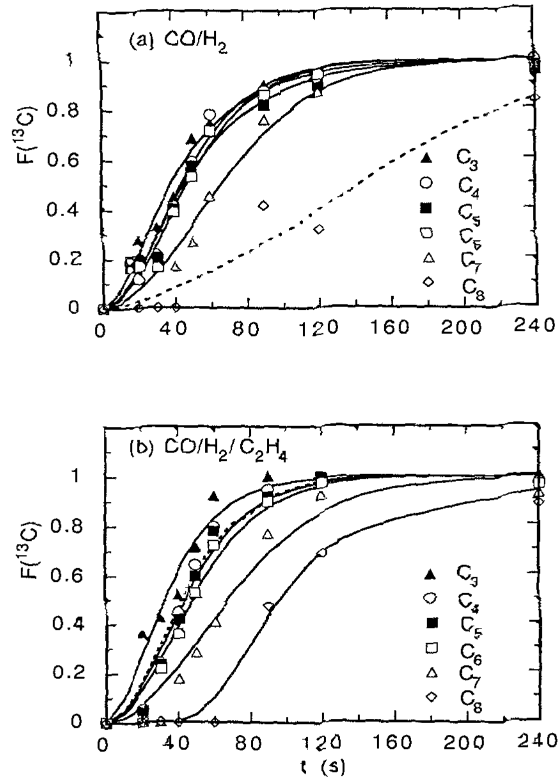

Fig. 2. $F_n(t)$ following (a) a switch from $^{12}CO/H_2$ to $^{13}CO/H_2$ at $t = 0$; (b) a switch from $^{12}CO/H_2/^{12}C_2H_4$ to $^{13}CO/H_2/^{12}C_2H_4$ at $t = 0$. Reaction conditions: $T = 463$ K; $H_2/CO = 3$.

products. Fig. 2b 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-labeled, and consequently, the steady-state value of

Table 2
Fraction of ^{12}C-labeled carbon in the C_3–C_8 products observed during steady-state reaction in a 1.2% $^{12}C_2H_4$/10% ^{13}CO/30% H_2/58.8% He mixture

Carbon number n	$F_n'(\infty)$ (expt.)	$F_n'(\infty)$ (theor.) [a]	$F_n'(\infty)$ (theor.) [b]
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

[a] Based on eq. (1), taking $f_i = 1.0$ and $f_m = 0$.
[b] Based on eq. (1), taking $f_i = 1.0$ and $f_m = 0.45$.

the ^{13}C fraction after 10 min in $^{13}CO/H_2/He/^{12}C_2H_4$ is used to normalize $F_n(t)$.

Table 2 lists values of $F_n'(\infty)$ for $n = 3–8$, where $F_n'(\infty)$ is the fraction of ^{12}C-labeled carbon in the products under steady-state reaction conditions in $^{13}CO/H_2/He/^{12}C_2H_4$ (i.e. after 10 min of reaction). The value of $F_2'(\infty)$ is not listed because the C_2 products were virtually 100% ^{12}C-labeled, as a consequence of the high concentration of $^{12}C_2H_4$ in the feed. Table 2 shows that as n increases from 3 to 8, $F_n'(\infty)$ decreases from 0.79 to 0.57.

4. Discussion

The results presented in figs. 1 and table 1 demonstrate that ethylene readily incorporates into the C_1 and C_{3+} products of FTS over Ru/TiO_2. The extent of ethylene incorporation increases in rough proportion to the ethylene concentration, and the extent of C_2H_4 hydrogenation to C_2H_6 decreases. These observations are qualitatively consistent with those reported in earlier studies of silica- and alumina-supported Ru [2,9–11,14,15].

During FTS, a major portion of the Ru surface is covered by adsorbed CO [16]. H_2 and C_2H_4 have heats of adsorption significantly lower than that of CO and, hence, must compete with CO for the vacant sites [17]. The large degree of C_2H_4, incorporation even at low gas concentrations together with the observations of Jordan and Bell [10] that the degree of C_2H_4 incorporation increases with increasing H_2/CO ratio at constant CO partial pressure, suggests that C_2H_4 enters into the FTS process via the following reactions:

$$C_2H_{4,g} \rightleftharpoons C_2H_{4,s}, \tag{I}$$

$$C_2H_{4,s} + H_s \rightleftharpoons C_2H_{5,s}. \tag{II}$$

In this scheme, $C_2H_{4,s}$ is a weakly bound, mobile precursor. The reaction of $C_2H_{5,s}$ with additional H_s can lead to C_2H_6 and CH_4, the latter product arising as a result of hydrogenolysis. The occurrence of reaction II and the subsequent processes leading to CH_4 and C_2H_6 should lower the surface coverage of H_s, relative to that in the absence of C_2H_4 addition. Such an effect could explain the reduction in the conversion of CO to hydrocarbons, which requires the dissociation of CO followed by the hydrogenation of the resulting C_s to produce $CH_{x,s}$ species. A reduction in the coverage of H_s would also explain the observed increase in the olefin to paraffin ratio upon ethylene addition.

The results shown in table 2 indicate that in the presence of 1.2% C_2H_4, a large fraction of the products are ^{12}C-labeled. 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, reflecting the fraction of ^{12}C 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 2 shows the results of this calculation. Comparison with the experimental values of $F_n'(\infty)$ reveals that the predicted decrease in $F_n'(\infty)$ with n is too rapid.

A slower decrease in the fraction of ^{12}C-labeled 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., $CH_{2,s}$). If it is assumed that the fraction of ^{12}C-labeled C_1 monomer is f_m, and that the fraction of C_2 initiators in the C_{3+} product is f_i, then $F_n'(\infty)$ can be written as

$$F_n'(\infty) = \frac{1}{n}\left[2f_i + (n-2)f_m\right]. \tag{1}$$

A multiple-regression of eq. (1) over the data for F_n' ($n = 3$–8) yields values of $f_i = 1.03$ and $f_m = 0.45$. This indicates that every product molecule contains a $^{12}C_2$ initiator unit, and that 45% of the monomer pool is ^{12}C-labeled. The results shown in table 1 indicate that the calculated isotopic compositions agree reasonably well with those observed.

The values of f_i and f_m determined from the results presented in table 1 can be compared with values of these parameters estimated from the data presented by previous investigators. In the work of Kobori et al. [9], $^{12}C_2H_4$ was added to a 2/1 $H_2/^{13}CO$ feed mixture. Based on the reported isotopic distributions in the C_3 and C_4 products, the value of f_i is calculated to be 0.86, from which it can be estimated that $0.5 < f_m < 0.6$. Consistent with the estimate of f_m is the observation that 59% of the CH_4 is ^{12}C-labeled. In studies reported by Mims et al. [11], $^{12}C_2H_4$ was added to a 2/1 $H_2/^{13}CO$ feed mixture. The values of f_i and f_m determined from their data are 0.75 and 0.52, respectively. It is, therefore, evident that the present results, together with those of Kobori et al. [9] and Mims et al. [11], clearly demonstrate the strong influence of small amounts of C_2H_4 on the initiation and propagation of hydrocarbon chains.

Nowak et al. [18] and Jordan and Bell [10] have proposed that in the presence of C_2H_4, chain growth might occur via both C_1 and C_2 monomer units. The data reported here suggest that C_2 units are not efficient in chain propagation. As shown in fig. 2, the addition of 1.2% C_2H_4 has virtually no effect on the dynamics of ^{13}C incorporation into the products, relative to that observed in the absence of C_2H_4 addition. This indicates that the mechanism and dynamics of chain growth are virtually the same in the presence and absence of C_2H_4, even though in the latter case, 54% of the C_{3+} products derive from C_2H_4. Krishna and Bell [12] have recently demonstrated that in the absence of C_2H_4 addition, isotopic tracer transient response curves similar to those presented in fig. 2 can be attributed to chain growth solely through C_1 monomer units.

A second argument against the participation of C_2 species in the chain growth process can also be given. If C_2 species were more efficient chain propagation units than C_1 species, the products with an even number of carbon units should contain more ^{12}C than the adjacent odd number products. The data presented in table 2 demonstrates that this is not the case inasmuch as the value of $F_n'(\infty)$ decreases monotonically with increasing n. Moreover, the data shown in fig. 2 indicate that the dynamics of carbon incorporation into the growing chains is the same with and without the addition of C_2H_4. These observations lead to the conclusion that C_2 species are much less effective chain propagation units than C_1 species, as suggested earlier by Mims et al. [11].

5. Conclusions

Isotopic tracer studies have shown that ethylene can act as an effective chain initiator and a source of C_1 building units during Fischer–Tropsch synthesis over Ru/TiO_2. When 1.2% C_2H_4 is added to a 3/1 H_2/CO mixture at 1 atm and 473 K, 100% of the hydrocarbon chain are initiated by adsorbed C_2H_4, and 45% of the C_1 species involved in chain propagation derive from C_2H_4. The added C_2H_4 causes an increase in the overall rate of hydrocarbon formation and a decrease in the rate of CO consumption. No evidence is found for the participation of C_2 units in the propagation of hydrocarbon chains.

Acknowledgement

This work was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract DE-AC03-76SF00098.

References

[1] R.B. Anderson, *The Fischer–Tropsch Synthesis* (Academic Press, New York, 1984).
[2] C.S. Kellner and A.T. Bell, J. Catal. 70 (1981) 418.
[3] D. Stern, H. Heinemann and A.T. Bell, Chem. Eng. Sci. 40 (1985) 1917.
[4] C.A. Mims, L.E. McCandlish and M.T. Melchior, Catal. Lett. 1 (1988) 121.
[5] C.A. Mims, L.E. McCandlish and M.T. Melchior, *Proc. 9th Int. Congress of Catalysis*, Vol. IV, (1988) p. 1992.
[6] E. Iglesia, S.C. Reyes and R.J. Madon, J. Catal. 129 (1991) 238.
[7] R.J. Madon, S.C. Reyes and E. Iglesia, J. Phys. Chem. 95 (1991) 7795.
[8] F.A.P. Cavalcanti, R. Oukaci, I. Wender and D.G. Blackmond, J. Catal. 123 (1990) 270.
[9] Y. Kobori, H. Yamasaki, S. Naito, T. Onishi and K. Tamaru, J. Chem. Soc. Faraday Trans. I 78 (1982) 1473.
[10] D.S. Jordan and A.T. Bell, J. Phys. Chem. 90 (1986) 4797.
[11] C.A. Mims, J.J. Krajewski, K.D. Rose and M.T. Melchior, Catal. Lett. 7 (1990) 119.
[12] K.R. Krishna and A.T. Bell, J. Catal., in press.

[13] R. Snel and R.L. Espinoza, J. Mol. Catal. 43 (1987) 237.
[14] A.A. Adesina, R.R. Hudgins and P.L. Silveston, App. Catal. 62 (1990) 295.
[15] S.R. Morris, R.B. Hayes, P.B. Wells and R. Whyman, J. Catal. 96 (1985) 23.
[16] P. Winslow and A.T. Bell, J. Catal. 86 (1984) 186; 91 (1983) 142; 94 (1985) 385.
[17] G.A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, Ithaca, 1981).
[18] S. Nowak, R. Madon and H.J. Suhl, J. Chem. Phys. 74 (1981) 6083.