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^{13}C-tracer study of the Fischer–Tropsch synthesis: another interpretation

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Abstract

The ^{13}C-tracer results from the introduction of $^{13}C_2H_4$ into syngas prior to conversion with a rhodium catalyst have been used to support a surface vinyl mechanism for Fischer–Tropsch synthesis. The results were first interpreted by a mechanism that involved a decrease in ^{13}C species on the surface as the carbon number increased. This model is shown to be incorrect. Considering only the ^{13}C-labeled products, the data are consistent with earlier tracer studies showing that the added $^{13}C_2H_4$ initiates chains. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Tracer; Syngas; Fischer–Tropsch synthesis

1. Introduction

Applications of isotopic tracer techniques have played important roles in developing and understanding of the mechanism for the Fischer–Tropsch (FT) synthesis. Among the first applications of ^{14}C in FT studies by Kummer et al. [1], ^{14}C-labeled iron carbide catalysts were used to show that the formation of bulk iron carbide and its subsequent hydrogenation, as proposed by Fischer and Tropsch [2], was not correct. Subsequent studies by Emmett and coworkers [3–13] using several ^{14}C-labeled compounds provided support for the oxygenate mechanism developed primarily at the US Bureau of Mines [14]. The FT products with carbon numbers larger than the labeled compound added as a tracer in the syngas feed, observed in these early studies by Emmett and coworkers, contained essentially the same amount of label/mol as the added labeled alcohol or olefin. Later studies, utilizing both gas and liquid chromatography to isolate pure hydrocarbon fractions of higher carbon-number alkanes produced data that agreed with those of Emmett and coworkers for the lower carbon number compounds (C_2–C_4); however, it was found that the molar radioactivity of the higher carbon number hydrocarbons (C_8–C_{22}) rapidly decreased with increasing carbon number [15–22]. The data obtained in the latter studies were consistent with the FT products produced using promoted iron catalysts formed by two independent chain growth processes; however, the latter data indicated that the decrease was due to accumulation of heavier products that were produced prior to the addition of the labeled compound.

Maitlis and coworkers [23–50] have published extensively on the mechanism of the C–C bond formation during the homogeneous and heterogeneous catalysis of the FT process. The heterogeneous catalysis studies have utilized several ^{13}C-labeled molecules, including those that could form a surface vinyl group and a rhodium catalyst. The authors reported data in Fig. 4 of Ref. [39] (our Fig. 1) which showed that the $^{13}C_2$ incorporation decreased as the carbon number of the product increased, and to explain their findings, they offered the following:

> “The calculation can be illustrated by the following example. If it is assumed that initially 20% of the

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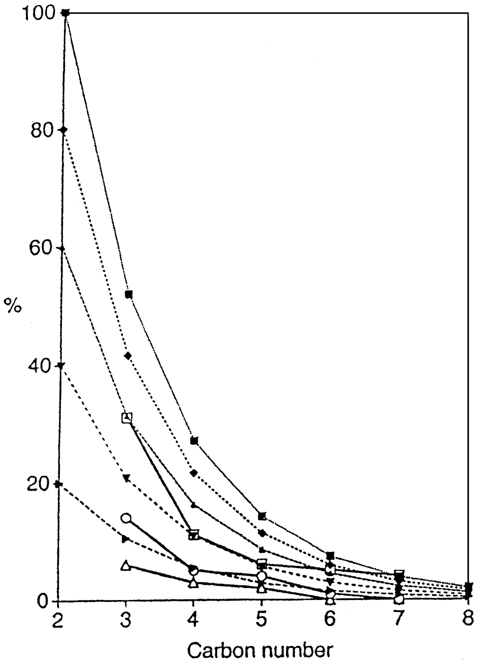

Fig. 1. Comparison between calculated $^{13}C_2$ incorporation assuming different initial surface concentrations of $^{13}C_2H_3$ (dotted lines: (···■···) 100%, (···◆···) 80%, (···▲···) 40%, (···▶···) 20%) and experimental $^{13}C_2$ incorporation derived from vinyl probes (bold lines (—□—) $^{13}C_2H_3Br$, (—○—) $(^{13}C_2H_3)_4Si$; (—◇—) $^{13}C_2H_4$): plot of percentage of coupled products that are $^{13}C_2$-labeled (*y* axis) against carbon number (*x* axis).

> surface vinyl is $^{13}C_2$-labeled (i.e., $[A_{n-1}]$=20%) and that α=0.52, then 52% of $^{13}C_2H_3$ will undergo propagation with methylene, and the amount that becomes incorporated into propenyl will be 0.52×20%=10%. Therefore, 10% of propene will be $^{13}C_2$-labeled. Similarly 52% of $^{13}C_2$-labeled propenyl will undergo homologation to form $^{13}C_2$-labeled but-1-enyl, and 5% of but-1-ene will be $^{13}C_2$-labeled (i.e., 0.52×10%=5%), and so on. This calculation can be done for different assumptions of initial $^{13}C_2$ surface vinyl."

Because of the complexity of the experiments and the data produced in the studies by Maitlis and coworkers, in this paper we shall refer only to the data produced during the addition of ^{13}C-labeled ethene. In the following, we offer another interpretation of the data and show that the assumptions of the surface of isotopically labeled surface species assumed in the above quote are not valid.

2. Discussion

The experimental procedures used for the synthesis and product analysis in the work by Maitlis and coworkers are not provided in detail. For example, the following is provided in [39]:

> "The products of the reaction were either sampled directly from the gas stream and analyzed by gas chromatography or collected in a liquid-nitrogen trap and analyzed by GC–MS. The latter method was used to collect enough of the higher molecular weight products for detection and GC–MS analysis. For the runs with probes, the products were analyzed by both GC and GC–MS before, during and after probe additions. A background GC was initially obtained to show the distribution of products and activity. After a period of 1.5 h, the probe molecule (e.g., $^{13}C_2H_4$ (BOC) as 6×280 μl pulses at 5 min intervals) was injected into the feed gas stream through a septum. A GC analysis was performed after the last injection. After a further 1.5 h period a final GC was carried out to ensure that the catalyst had returned to its initial unperturbed state. In each case a 250 μl sample was collected for analysis in a gas syringe over 5 s at a predetermined time after injection of the final pulse."

It appears that either sampling technique, collecting a gas sample after some period following the addition of six pulses or the collection of a sample in the liquid nitrogen trap during the period of pulse additions, will result in the dilution of the products produced during the brief period when the pulse traverses the catalyst bed with those products formed when only the syngas was present. The dilution by products produced when ^{13}C-labeled vinyl precursor was absent will be greater when the sample is collected in the liquid-nitrogen trap and presumably this was the case for the data presented in Fig. 4 described above, since it contains products through C_7. In any case, it is apparent that the products analyzed by Maitlis and coworkers will contain products formed during periods when $^{13}C_2H_4$ was not being added.

Maitlis and coworkers recognize that there will be $^{13}C_2$ and $^{12}C_2$ surface species present during the labeling portion of their studies. A calculation procedure that differs from the one described above by Maitlis and coworkers is required. If initially 20% of the surface vinyl species is $^{13}C_2$-labeled and if α=0.52, as assumed by Maitlis et al., then 80% of the surface vinyl species must be $^{12}C_2$. If, as assumed, 52% of the $^{13}C_2$ species undergoes propagation with a methylene derived from CO, the amount of $^{13}C_2$ that becomes incorporated into propenyl surface species is 0.52×20%=10.4%. Likewise, 52% of $^{12}C_2$ will also undergo propagation with methylene and the amount of $^{12}C_2$ propenyl will be 0.52×80%=41.6%. Therefore, the percentage of $^{13}C_2$-labeled propenyl will be 20% (i.e., 10.4%/(10.4%+41.6%)=20%). If the assumption that the surface vinyl species (or any other surface C_2 species) acts only as an initiator of chains is valid, the percentage of the $^{13}C_2$-labeled isotopomer of any higher carbon-number compound will be 20% in the above example — no more, no less. This example can be generalized for any isotope tracer study of the FT synthesis that obeys an Anderson–Schulz–Flory chain growth mechanism

$$\frac{L_{n-1}}{L_{n-1}+P_{n-1}}=\frac{L_n}{L_n+P_n}=\frac{L_{n+1}}{L_{n+1}+P_{n+1}}=C \quad (1)$$

where L is the amount of labeled compound produced during the tracer experiment, P the amount of unlabeled compound produced during the same period and C is a constant that is determined by the initial surface coverage of the labeled species.

A change in the α value of the FT reaction will not change the percentage of $^{13}C_2$ label in a higher carbon-number compound. For example, if the α value for the reaction was 0.4 rather than 0.52 as used in the above example, the percentage of $^{13}C_2$-labeled isotopomer will still be 20% (i.e., $^{13}C_2$-labeled=0.4×20%=8%; unlabeled, 0.4×80%=32% and the percentage of $^{13}C_2$-labeled=8%/(8%+32%)=20%). Since the surface coverage will be directly related to the isotopic distribution of the products that desorb from the catalyst surface, the molar label in each product must be the same as indicated in Eq. (1).

An increase in the molar label with carbon number is possible. If, e.g., some or all of the added $^{13}C_2$ was converted to a $^{13}C_1$-surface species, then the molar activity of C_{n+1} would be larger than that of C_n. However, this situation does not apply for the data presented by Maitlis and coworkers, by Emmett and coworkers, and by our studies. In all three instances, when labeled-ethene is added, labeled-methane was too small to detect. In our data as well as in those of Maitlis and coworkers, the molar radioactivity decreases with increasing carbon number.

If the fraction of labeled surface species does not change, then the molar activity can decrease with increasing carbon number only if there is an additional source of the unlabeled isotopomer. If we designate the amount of the isotopomer from an additional source as Δ, Eq. (1) becomes

$$\frac{L_{n-1}}{L_{n-1}+P_{n-1}+\Delta_{n-1}}=\frac{L_n}{L_n+P_n+\Delta_n}=\frac{L_{n+1}}{L_{n+1}+P_{n+1}+\Delta_{n+1}} \quad (2)$$

In considering the data generated in the studies by Maitlis and coworkers, it is better to ask, “Why does the relative amount of ^{12}C-isotopomer fraction increase as the carbon number increases?”

In most tracer studies of the FT synthesis, the unlabeled syngas conversion is conducted until the catalytic activity has stabilized and then the labeled compound is added for some time period. Usually the products are collected during the period of label addition. Following this procedure, the products collected will consist of three fractions: (1) the products derived from the labeled compound, (2) the products from the normal FT synthesis that are derived from the unlabeled syngas, and (3) any products formed from unlabeled synthesis gas during the period of activity stabilization or periods when the labeled compound is not added. These fractions are designated L, P and Δ, respectively, in Eqs. (1) and (2). In practice, the higher molecular weight, higher-boiling alkanes will remain in the reactor for a longer time than the lower-boiling compounds. This means that the lower molecular weight products will exit the reactor very quickly and the labeled fraction of these lower molecular weight products will be little affected by accumulation. On the other hand, the average residence time will increase with carbon number and the higher carbon number products may be affected by accumulation of unlabeled products. The accumulation effect will be more serious in larger size reactors (e.g., 1 l autoclaves containing 200–500 ml of liquid hydrocarbons) than in small plug flow reactors with a smaller holdup of liquid products; likewise, a higher pressure for the synthesis will result in a greater impact of product accumulation. For example, during a 5 h period when deuterated ethanol was added to the synthesis gas fed to a 1 l CSTR, the C_{18} alkane product that had accumulated in the reactor was approximately 60 times greater than the C_{18} produced during the 5 h period [51]. As another example, ^{14}C-labeled ethanol was present in the syngas feed to a 1 l CSTR for a 5 h period; following the period of tracer addition liquid samples were withdrawn every 24 h. The liquid sample collected on the third day after terminating the ethanol tracer addition contained about 4% of the total radioactivity present in the labeled compound that was added. Thus, product accumulation within the reactor must be taken into account when utilizing data from tracer studies. Furthermore, if $\Delta_{n-1}<\Delta_n$, Eq. (2) becomes

$$\frac{L_{n-1}}{L_{n-1}+P_{n-1}+\Delta_{n-1}} > \frac{L_n}{L_n+P_n+\Delta_n} > \frac{L_{n+1}}{L_{n+1}+P_{n+1}+\Delta_{n+1}}\cdots \tag{3}$$

In this case, the molar radioactivity or mole percent of ^{13}C or ^{14}C-labeled compound will decrease with increasing carbon number. It will be shown below that the data reported by Maitlis and coworkers for $^{13}C_2H_4$ addition are consistent with disproportionate accumulation impacting the results.

One can use the percentage of the ^{12}C-isotopomer of a compound to roughly estimate the effect of accumulation on the experimental results. If it is assumed that the probe $^{13}C_2H_4$ serves only as an initiator of chain growth, the percentage of ^{12}C-isotopomer of each compound will be the same. Assuming that there was no ^{12}C-propane in the reactor before adding the tracer, the percentage of the ^{12}C-isotopomer for each carbon-number compound should be the same as ^{12}C-propane, and have a value of 89%. For ^{12}C-heptane, the value is 97%, 8% more ^{12}C-heptane in the sample analyzed than it should have been based on ^{12}C-propane. The higher percentage of ^{12}C-heptane is due to the accumulation effect. The data reported by Maitlis and coworkers indicate that as the carbon number increases, the amount of ^{12}C-isopotomer of each component increases. One could devise ways to make an estimation of this as was done by assuming that there is no accumulation of the propane. However, this problem can be avoided by utilizing the data in another way.

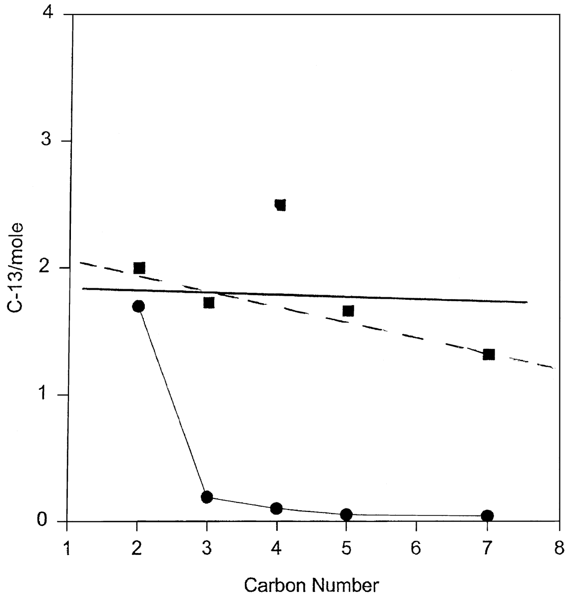

Fig. 2. The ^{13}C/mol in alkane in $^{13}C_2H_4$ tracer study run over a Rh/Ce/SiO_2 catalyst (data from Table 2C of Ref. [2]): (●) ^{12}C isomer of each compound was included; (■) ^{12}C isomer of each compound was eliminated.

Our approach utilizes only the products that contain ^{13}C for all carbon-number products. Any products that accumulate in the reactor will not contain ^{13}C apart from that of the natural abundance of this isotope and the data have been corrected for the natural abundance. Thus, all ^{12}C-isotopomers of the compounds are eliminated from consideration and the distribution of ^{13}C-labeled products is calculated. The ^{13}C/mol in the alkanes produced in the study using the $^{13}C_2H_4$ tracer were calculated from the data given in Table 2c of Ref. [39] and are plotted in Fig. 2 as well as the distribution when the data include the ^{12}C-isotopomer. When the ^{12}C-isotopomers of each carbon number are included, the value of ^{13}C/mol for propane is 0.21 and the value declines to 0.04 for heptane. When only the ^{13}C-containing isotopomers are considered, the value of ^{13}C/mol is close to 2 for the alkanes except for heptane (solid line, Fig. 2), which has a value of 1.3. The ^{13}C/mol for the 1-alkenes, using the data from Table 2c of Ref. [39] are plotted in Fig. 3 and have values that are similar to those for the alkanes.

If the $^{13}C_2$ species derived from $^{13}C_2H_4$ is an initiator and if its behavior is the same as the $^{12}C_2$ species

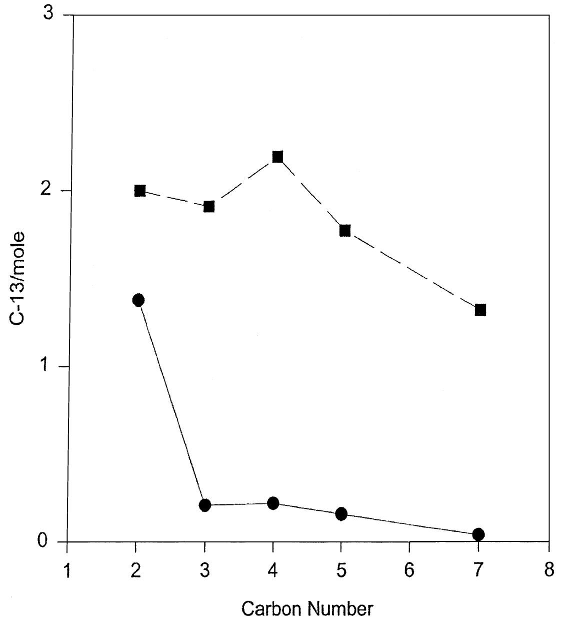

Fig. 3. The ^{13}C/mol in alk-1-enes in $^{13}C_2H_4$ tracer study run over a Rh/Ce/SiO$_2$ catalyst (data from Table 2C of Ref. [2]): (●) ^{12}C isomer of each compound was included; (■) ^{12}C isomer of each compound was eliminated.

derived from CO, the ^{13}C/mol for each compound must be the same. When considering just the ^{13}C containing isotopomers, the ^{13}C/mol must be close to 2, since the initiating ethene contains close to two ^{13}C per molecule. The data for the isotopomers of the alkanes have a value that is about 2 (solid line, Fig. 2), and may decrease slowly with increasing number. Furthermore, the value for C$_4$ is high compared to the other alkanes; the higher value for C$_4$ indicates that some dimerization of ethene to produce C$_4$ occurs (perhaps 25% of the C$_4$ that is produced). The ^{13}C/mole values for the alkenes (Fig. 3) are nearly constant with a value of 2 as required for chain initiation by $^{13}C_2H_4$. Again, the high value for C$_4$ indicates that some of the C$_4$ is formed by dimerization of $^{13}C_2H_4$. Thus, with our calculation there is an excellent agreement of the experimental data with the value expected for chain initiation by $^{13}C_2H_4$. This is in marked contrast to the calculated values when both the ^{13}C isotopomers and the ^{12}C isotopomers are included in the calculation. In fact, one can reach the same conclusion by comparing the data in Table 2c of Ref. [39]. The major isotopomer of each carbon-number compound, except C$_4$, is the one containing two ^{13}C which clearly demonstrates the role of ethylene as an initiator.

Maitlis and coworkers did not provide an estimate of the accuracy for their GC–MS measurements. We have used GC–MS measurements to obtain the relative deuterium content of hydrocarbons in the carbon-number range that Maitlis used. In our studies, we obtained the isotopomer content from the GC–MS measurements and compared these to the content of the mixtures that were prepared by accurately weighing the added components. When the relative ratio of two isotopomers fall in the range 1–30, the GC–MS data are the same as the value obtained from weighing with a standard deviation of 0.94 or better [52]. As the ratio becomes greater than 30, the experimental error increases. Thus, if one isotopomer is present at the 90% level and another is 3% or less, the experimental error for the 3% isotopomer will be greater than $+0.2\%$ and the data should not be utilized to reach conclusions. If the data obtained with deuterated isotopomers can be extended to those for ^{13}C isotopomers, some of the data obtained by Maitlis should not be utilized. For instance, the relative ratio of ^{12}C-heptane/^{13}C-heptane in the run with $^{13}C_2H_4$ is 90. This ratio suggests that the GC–MS data for heptane is very uncertain.

The role of ethene and the C$_2$ species derived from it in the FT synthesis has been controversial. Some, based on ^{14}C-tracer studies, consider it to serve as a chain initiator (e.g., [53–57]), while others consider it to function as an initiator as well as a propagator [19,58]. In fact, the reincorporation of alkenes into the FT synthesis has been involved to account for the positive deviation of the higher carbon-number products from the ASF distribution (e.g., [59,60]). The experiments conducted by Maitlis and coworkers utilizing ^{13}C provide additional evidence for the role of the C$_2$ species derived from ethene in the FT reaction mechanism. Maitlis and coworkers [39] conclude that, “The data show that the degree of ^{13}C incorporation decreases with increasing number of carbons in the hydrocarbon product. This is consistent with the C$_2$ species being involved in chain initiation rather than chain propagation”. The data they obtained are consistent with this conclusion but the logic they used to reach the quoted conclusion is not valid. Using a valid method for interpreting the mechanistic implications of the data, it is concluded that the dominant role of added ethylene is to initiate chain growth. A valid method of utilizing the data generated by Maitlis and coworkers shows that the amount of ethene incorporated provides a constant value of ^{13}C/mol and this ratio has a value of 2 as required when only the products are derived by initiation by $^{13}C_2H_4$ for both the alkene and alkane products. Thus, the data generated by Maitlis and coworkers are consistent with the body of evidence that shows that the initiation of chain growth by an added isotopically labeled compound leads to a constant isotope/mol value for all higher carbon number compounds. Negative deviations from the constant value are considered to be due to dilution by disproportionate accumulation of unlabeled products. In the case of Maitlis and coworkers, the accumulation is most likely due to the products produced from the unlabeled syngas in the six periods between the addition of six pulses of ethene addition. In the case of Tau et al. [19] the decrease in isotopic label/mol with increasing carbon number is due to the accumulation of unlabeled compounds produced prior to the period of the addition of the isotopic labeled compound in the large volume of reactor solvent.

Maitlis and coworkers consider the added ethene to adsorb as a vinylic species, $H_2C{=}CH–$. However, direct experimental evidence is not provided for this adsorbed species. The vinylic C–H bond rupture is a high energy process and it is more likely that the bonding involves initially the π-bond of ethene. In many catalytic processes the π-bonded alkene is viewed to react with an adsorbed hydrogen, either during adsorption (Eley–Rideal mechanism) or following adsorption (Langmuir–Hinshelwood mechanism), to form an adsorbed alkyl group, $CH_3CH_2–$. An alternative could be a rearrangement to produce an adsorbed $CH_3CH{=}$ group. Either of these adsorbed species should require less energy to form than the adsorbed $CH_2{=}CH–$ species. In any event, it appears that the dominant role for ethene added to the syngas is to initiate chains with minor contributions to oligomerization and/or propagation processes.

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