 Reaction of ethylene over a typical Fischer-Tropsch synthesis Co/TiO₂ catalyst

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1 INTRODUCTION

Fischer-Tropsch synthesis (FTS) is an important technology used to convert syngas derived from coal/gas/biomass into clean transport fuels or other valuable organics.¹⁻⁸ FTS is generally regarded as a polymerization-like reaction. The products of FTS are a wide range of hydrocarbons, consisting of mainly olefins and paraffins, with a small amount of oxygenates. The Anderson-Schulz-Flory (ASF) equation is used to describe the FT product distribution; however, deviations from the ideal ASF distribution, such as a higher yield of C₁, and a lower yield of C₂, have been observed.⁹,¹⁰ Many theories have been proposed to explain the deviation, and secondary reactions of olefins is considered as a reasonable explanation.¹¹⁻¹⁴ Therefore, it is interesting to investigate the reaction of C₂H₄ under typical FTS operating conditions (similar space velocity, temperatures, and pressures).

Abstract
In order to identify the potential reaction paths of C₂H₄ and their product distribution in Fischer-Tropsch synthesis (FTS), a series of experiments were designed over a Co/TiO₂ catalyst in the absence of CO. C₂H₄ did quickly react with H₂ to produce C₁⁻₆ products under Fischer-Tropsch (FT) reaction conditions. Although the dominant reaction is C₂H₄ hydrogenation to ethane, changing the reaction conditions (temperature and partial pressure of reactants) can lead to the other reaction pathways being enhanced, resulting in varying product selectivity to both linear and branch olefins and paraffins. Possible reaction pathways had been summarized and discussed, which including C₂H₄ reaction to ethylidene followed by dimerization; C₂H₄ insertion into C₂ surface species and dimerization and C₄ decomposition and/or direct C₂ hydrogenolysis. Furthermore, the products obtained from C₂H₄ reactions were fit to a typical FTS product distribution, which indicate that both the chain growth initiators and monomers are not necessarily only derived from hydrogenation of CO but also from the secondary reactions of olefins.

KEYWORDS
cobalt catalysts, Fischer-Tropsch synthesis, product distribution, reactivity of C₂H₄
The olefin product produced by the FTS may re-adsorb on the catalyst surface and undergo secondary reactions. The effect of co-feeding low concentrations of C₂H₄ to the FTS reaction system has been studied previously, in order to investigate the reactivity of the olefins in the FTS reaction. Different secondary reactions of olefins have been reported, and in particular hydrogenation, isomerization (bond shift reaction), hydrogenolysis, reinsertion into chain growth as monomers, initiation of hydrocarbon chain, and hydroformylation have been observed.

The reactivity of C₂H₄ under FTS conditions has been reported for both Fe-based and Co-based catalysts. Schulz et al. found that the conversion of C₂H₄ was less than 80% for iron-based catalysts, while almost all the C₂H₄ was converted (conversions over 90%) when using cobalt-based catalysts. In addition, hydrogenation of C₂H₄ is the dominant reaction under all reaction conditions. Later, reabsorption and insertion of C₂H₄ to form longer carbon chain products on Co-based catalysts were reported. Furthermore, a decrease in CH₄ selectivity was found when C₂H₄ was co-fed, which was considered due to the competitive reaction between CO methanation and C₂H₄ incorporation with the C₁ species.

Some studies focused on the hydro-polymerization of C₂H₄ at very low partial pressures of CO over supported Co-based catalysts. It is reported that the C₂H₄ in the feed was completely consumed, and the CO partially hydrogenated to generate longer chain hydrocarbons. Kokes et al. found that a large number of C₂H₄ dimerization products (C₄), especially olefins, were formed when hydrogen was deficient. They proposed that an adsorbed intermediate of 1,1-σ-ethylidene, converted by 1,2-diadsorbed C₂H₄ with hydrogen assistance, could polymerize to form C₂H₄ dimers. However, most of the studies reported were carried out under typical FT reaction conditions, such as low conversion and/or atypical pressures. More recently, some studies on co-feeding C₂H₄ to an FTS reaction system were carried out using a combined quantitative in-situ FTIR and online gas chromatography. The researchers found that co-feeding C₂H₄ did not alter the selectivity of the product, but changed the chain length of the adsorbate on the catalyst surface.

In summary, the types of FTS catalyst, and the operating conditions (temperature, residence time, and partial pressure of the reactants and products) had a significant impact on the secondary reactions of C₂H₄. Researchers have found that it was difficult to investigate certain aspects independently due to the system complexity and number of the reactions occurring in FTS. In addition, some reaction pathways may be obscured when many reactions are occurring simultaneously. In order to fully understand the reaction pathways of the olefin, we suggest simplifying the complex system and investigating one aspect at a time.

In this work, several groups of experiments were carried out over a FT Co-based catalyst, in the absence of CO, under typical FT reaction conditions. First, mixtures of C₂H₄ and N₂ were fed to the reactor and later the feed was changed to mixtures of C₂H₄ and H₂. The effect of the feed gas ratio (C₂H₄/H₂) and the reaction temperatures on the reactivity of C₂H₄ and resulting product selectivity could be investigated without either the reactant CO or the FT by-products influencing the system.

2 Experimental Methods

2.1 Catalyst preparation

The catalysts used in this study (15 wt% Co supported on TiO₂) were prepared using the incipient wetness method. Co(NO₃)₂·6H₂O (Sigma Aldrich) was used as the metal precursor salt, and TiO₂ (Degussa P-25) was used as the catalyst support precursor. The TiO₂ paste was made by mixing TiO₂ with distilled water at a mass ratio of 1:1. After being dried at 120°C for 2 hours, the paste was calcined in a Muffle oven that was heated from room temperature to 400°C at a rate of 5°C/min and then maintained at 400°C for 6 hours. The support was crushed and sieved after calcination, and particles of which between 0.5 and 1 mm were selected for the impregnation step. 1 g of the support was measured out, and distilled water (0.8 mL) was gradually dropped onto the support until the surface was infiltrated. The pre-treated and selected TiO₂ support was impregnated with a Co(NO₃)₃ aqueous solution, with a Co metal loading of 15% by mass. Thereafter, the wet catalyst was dried at 120°C for 2 hours, and then calcined at 400°C for 6 hours. Catalyst information is summarized in Table 1.
### TABLE 1 Properties of the catalyst (15% Co/TiO₂) used in this work

| Catalyst | 15% Co/TiO₂ |
|----------|-------------|
| Particle size (mm) | 0.5-1 |
| Surface area (m²/g) | 42.92 |
| Pore volume (cm³/g) | 0.24 |
| Average pore diameter (nm) | 16.7 |

#### 2.2 Reaction procedure and product analysis

The fixed bed reactor used in this study had a 203.8 mm long stainless tube with an inner diameter of 8 mm. 1 g of catalyst was loaded into the reactor, and the catalyst was reduced at 350°C in pure H₂ (AFROX [African Oxygen] Ltd., 99.999%), for 4 hours at 30 mL/min and 1 bar gauge. After catalyst reduction, the reactor was cooled to a temperature below 100°C. Thereafter, three groups of experiments were conducted, as follows:

- **Group 1 (Run 1)**
  
  A normal FT reaction was conducted with a feed gas of H₂/CO/N₂ (H₂/CO = 2:1), at 30 mL/min, 200°C, and 20 bar (on gauge). This was used to test the catalyst performance during FTS. Thereafter, the reactor was purged with inert gas N₂.

- **Group 2 (Runs 2-4)**
  
  First, a feed of pure C₂H₄ was introduced into the reactor at 20 bar and the temperature was varied between 180°C and 220°C, while the total flow rate was maintained at 50 mL/min. Then, N₂ was co-fed into the reactor using various C₂H₄/N₂ ratios. The operating temperature was also varied from 180°C to 220°C while keeping the total pressure at 20 bar.

- **Group 3 (Runs 5-11)**
  
  H₂ was co-fed with C₂H₄ into the reactor at 20 bar and 180°C, 60 mL/min. The ratio of C₂H₄ to hydrogen was changed from 0.5 to 4.6. Thereafter, experiments were run at 2 different C₂H₄/H₂ ratios, namely, 0.8 (which we denote “Excess H₂”) followed by 4.8 (denoted “H₂ limiting”), and the operating temperature in the reactor was varied between 100°C and 250°C, to investigate the effect of the C₂H₄/H₂ ratio and temperature on C₂H₄ reactivity.

The reaction conditions are summarized in Table 2. The feed and tail gas were analyzed using an online Gas Chromatograph (GC, Agilent 7890B). A flame ionization detector (FID) was used to analyze the hydrocarbons, and two thermal conductivity detectors (TCD) were used to analyze H₂/N₂. The experimental results monitored by the GC indicated that the normal FT reaction (Run 1) stabilized after 13 hours (see in Figure 2); and the C₂H₄ hydrogenation reaction reached a steady state less than 2 hours for each run. The experimental results reported in the current work were the average values obtained between 17 and 23 hours for all the runs.

In the FTS experiment (Run 1), the feed gas flow rate was controlled by a mass flow controller (Brooks) and N₂ was used as an internal standard for the calculation of the results. The CO conversion (\(\%\)CO) and hydrocarbon selectivity (\(S_{Cn,1}\)) were calculated using the following equations:

\[
\%\text{CO} = \frac{(F_{\text{CO,in}} - F_{\text{CO,out}})}{F_{\text{CO,in}}} \times 100\% \\
S_{Cn,1} = \frac{n \times F_{\text{Cn,out}}}{(F_{\text{CO,in}} - F_{\text{CO,out}})} \times 100\% 
\]

During the reaction of ethylene (Runs 5-11), the flow rate of feed gas was controlled by a mass flow controller (Brooks) and the flow rate of the tailgas was measured using a bubble flow meter. The C₂H₄ conversion (\(\%\)C₂H₄) and hydrocarbons selectivity (\(S_{Cn,2}\)) were estimated using the following equations:

\[
\%\text{C₂H₄} = \frac{(F_{\text{C₂H₄,in}} - F_{\text{C₂H₄,out}})}{F_{\text{C₂H₄,in}}} \times 100\% \\
S_{Cn,2} = \frac{n \times F_{\text{Cn,out}}}{2 \times (F_{\text{C₂H₄,in}} - F_{\text{C₂H₄,out}})} \times 100\%.
\]
TABLE 2 Reaction conditions for all 11 runs

| Experiment | Feed            | Temperature °C | Total Pressure Bar (on gauge) | Total Flow ml/min | Feed partial pressure (bar) | C2H4 | H2  | N2  | C2H4/H2 |
|------------|-----------------|----------------|-------------------------------|-------------------|-----------------------------|------|-----|-----|---------|
| Run 1      | H2/CO/N2        | 200            | 20                            | 30                | H2/CO/N2 = 6:3:1 with no C2H4 |
| Run 2      | C2H4/N2         | 180 to 220     | 20                            | 50                | 21.0                        | 0.0  | 0.0 | 0.0 | N/A     |
| Run 3      | C2H4/N2         | 180 to 220     | 20                            | 50                | 16.8                        | 0.0  | 4.2 | N/A |
| Run 4      | C2H4/N2         | 180 to 220     | 20                            | 50                | 10.5                        | 0.0  | 10.5| N/A |
| Run 5      | C2H4/H2         | 180            | 20                            | 45                | 7.0                         | 14.0 | 0.0 | 0.5 |
| Run 6      | C2H4/H2         | 180            | 20                            | 52.5              | 9.0                         | 12.0 | 0.0 | 0.8 |
| Run 7      | C2H4/H2         | 180            | 20                            | 60                | 10.5                        | 10.5 | 0.0 | 1.0 |
| Run 8      | C2H4/H2         | 180            | 20                            | 45                | 14.8                        | 6.2  | 0.0 | 2.4 |
| Run 9      | C2H4/H2         | 180            | 20                            | 50                | 17.2                        | 3.8  | 0.0 | 4.6 |
| Run 10     | C2H4/H2         | 100 to 250     | 20                            | 52.5              | 9.3                         | 11.7 | 0.0 | 0.8 |
| Run 11     | C2H4/H2         | 110 to 250     | 20                            | 50                | 17.4                        | 3.6  | 0.0 | 4.8 |

Where: FC0.in and FC0.out are the CO molar flow rates of the feed gas and the tailgas, respectively (mmol/min), FC2H4.in and FC2H4.out are the ethylene molar flow rates of the feed gas and the tailgas, respectively (mmol/min), n is the carbon number of product Cn, and FCn.out is the molar flow rate of hydrocarbon product with carbon number n in tailgas (mmol/min).

2.3 | Catalyst characterization

The reducibility of the catalyst was measured by hydrogen temperature programmed reduction (H2-TPR). Two experiments were conducted:

1. Experiment 1: 50 mg of catalyst was loaded into the quartz reactor. A 5% H2/N2 reducing mixture, at a flow rate of 30 mL/min, was passed through the reactor. The temperature of the reactor was programmed to increase from room temperature to 700°C at a heating rate of 10°C/min.
2. Experiment 2: the same experimental procedure was followed as with experiment 1, the difference being that the reaction temperature increased from room temperature to 350°C at a rate of 10°C/min, and it was then maintained at 350°C for 1 hour. The H2 concentration during the reduction was measured using a thermal conductivity detector (TCD).

X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-2500 diffractometer, with Cu Kα radiation at 40 kV and 100 mA in a scanning range of 3°-80° (2θ). The diffraction peaks of the crystalline phase were compared with those of standard compounds reported in the JCPDS Date File.

The nitrogen adsorption-desorption experiment was measured using a Quantachrome Autosorb-1MP sorption analyser at −196°C. Before measurement, the samples were de-gassed at 200°C for at least 6 hours. The specific surface area (SBET) was calculated using the Brunauer-Emmett-Teller (BET) method (P/P0 < 0.1).

3 | EXPERIMENT RESULTS

3.1 | Catalyst characterization

The characteristic results of TPR and XRD are shown in Figure 1A-C. Figure 1A indicates that the catalyst starts to reduce at temperatures above 320°C. Figure 1B shows that the catalyst can be activated at 350°C. Based on the literature, there are two steps during the cobalt catalyst reduction process: (a) from Co3O4 to CoO, around 300°C; (b) from CoO to metallic
FIGURE 1 Characterization results for: A, H₂-TPR profiles with the reduction temperature increasing from room temperature to 700°C at a rate of 10°C/min; B, H₂-TPR profiles with the reduction temperature increasing from room temperature to 350°C (10°C/min) and then being maintained at 350°C for 1 hour; C, XRD patterns for 15% Co/TiO₂ before and after reduction; and D, TEM images of the catalyst.

Co, around 500°C.³⁶ As shown in Figure 1A,B, A and B represent these two reduction steps. It indicates at 350°C, at least part of Co₃O₄ reduce to metallic Co. The comparison of the XRD results for the fresh catalyst, before reduction and after reduction, at 350°C, is shown in Figure 1C. The pattern produced by the catalyst before reduction shows some sharp peaks, which may be due to the cubic Co₃O₄ (JCPDS65-3103). However, after reduction, the intensity of the Co₃O₄ peaks either disappears or is reduced. At the same time, certain Co (JCPDS15-0806) peaks appear. Although the signal of metallic Co is weak and difficult to distinguish from the noise, combined with the TPR result, it confirms that metallic Co exists in reduced catalysts. According to the BET results, the catalyst surface area is about 43 m²/g, the pore volume is 0.24 cm³/g, and the average pore diameter is 16.7 nm. (See Table 2.) All the characterization results show that the catalyst used in this experiment is a typical Co-based FTS catalyst. Figure 1D shows the TEM images of catalysts.

3.2 Confirming FTS reactivity of the Co catalyst

When the syngas (H₂/CO = 2:1) is introduced into the reactor, a typical product distribution of a Co-based FT catalyst¹³ is obtained (see Table 3 and Figure 8A). The CH₄ selectivity is high (16%), while the C₂ product selectivity is lower than that expected from an ideal ASF distribution. In addition, the C₃⁺ product distribution is consistent with an ASF distribution, with α-value = 0.82 (Figure 8A). Moreover, the total C₅⁺ selectivity is 65.03%. Figure 2 shows the CO conversion and methane selectivity with respect to time on steam (TOS). As can be seen, FTS stabilized at around 13 hours TOS. To avoid errors, the average value of results obtained between 17 and 23 hours after the experimental conditions are changed are used in Table 3 and Figure 8A. The experimental results clearly confirm that the catalyst used in this experiment is a typical FTS Co-based catalyst.³⁷

3.3 Feeding C₂H₄/N₂ to the reactor

In order to test if pure C₂H₄ could react under normal FT operating conditions, gas mixtures of C₂H₄/N₂ were fed to the reactor. N₂ is an inert gas with the function of adjusting the partial pressure of C₂H₄ to the reactor system. When the reactor was operated at 20 bars (on gauge) and 180°C, no product was detected by the online GC. The reaction temperature
was then increased from 180°C to 220°C, but product was still not detected. Adjusting the partial pressure of C2H4, by changing the molar ratio of C2H4/N2 in the feed mixture (Table 2), did not result in the C2H4 reacting. These results indicate that the C=C double bond of C2H4 could not open or break when only C2H4 (with or without an inert gas N2) is fed to the reactor. In other words, C2H4 itself does not easily react as a monomer to polymerize to form long chain hydrocarbons, without the assistance of other gases, such as H2.

3.4 | Feeding C2H4/H2 to the reactor

3.4.1 | Effect of C2H4/H2 molar feed ratio

The feed gas was switched to a mixture of C2H4/H2 with the reactor operating at 180°C and 20 bars gauge and the GC detected some short chain hydrocarbon products. The feed ratio was varied and the conversion of C2H4 and H2 and the product selectivity are plotted in Figure 3. Figure 3A shows that when C2H4/H2 < 1, C2H4 is completely converted. However, the conversion of H2 reaches more than 98% when C2H4/H2 ≥ 1, but the C2H4 conversion drops from 91% to 22%. (See Figure 3A.) The ethane selectivity decreases from 98.98% to 95.75%, when the C2H4/H2 ratio is increased from 0.5 to 1; thereafter the ethane selectivity does not change much as the C2H4/H2 ratio is increased above 1. In all cases, hydrogenation of C2H4 to ethane is the main reaction and this contributes to the high ethane selectivity (>95%). This is in line with published reports.6

Figure 3B,C shows:

1. When the C2H4/H2 ratio increases from 0.5 to 4.6, the paraffin product selectivity for C1, C3 and C4 increases, reaching a maximum at ratio of 0.8 and then decreases.
2. When C2H4/H2 ≥ 1, both C3 and C4 olefins (including the corresponding isomers) are produced, and the total yield of olefins is much higher than that of paraffins.
When the C$_2$H$_4$/H$_2$ ratio is increased from 1 to 4.6: the selectivity of total C$_4$ product increases from 2.2% to 2.8%; the selectivity of CH$_4$ and total C$_3$ product decreases from 0.5% to 0.1% and 1.5% to 0.3%, respectively.

Because C$_2$H$_4$ was the only carbon source in these experiments, the production of C$_1$ and C$_3$ indicates that the C-C bond ruptures to form odd carbon number products when co-feeding H$_2$. The selectivity of both CH$_4$ and C$_3$ decreases with increasing partial pressure of C$_2$H$_4$ (C$_2$H$_4$/H$_2$ > 1). This implies that few carbon chain products formed from the hydrocracking or demethylation reaction.
The major C₄ olefin under these reaction conditions was 2-butene. This phenomenon indicates that the production of 2-butene in FTS may come from the C₂H₄ dimerization reaction. In addition, with an increase in the partial pressure of C₂H₄, the selectivity of cis-2-butene increased, while the trans-2-butene yield decreased.

3.4.2 Influence of reaction temperature when C₂H₄/H₂ < 1 in the feed gas (H₂ in excess)

As described earlier, the product distribution changes with C₂H₄/H₂ ratio. To investigate the effect of temperature on the reaction of C₂H₄ with H₂, two groups of experiments were carried out: one using the feed gas with a molar ratio of C₂H₄/H₂ = 0.8 (excess H₂); the other with C₂H₄/H₂ = 4.8 (H₂ limiting- see next section). The term “excess” of “limiting” refers to the hydrogenation reaction, where a ratio C₂H₄/H₂ = 1 would be the correct ratio if all the C₂H₄ reacted to ethane. Figure 4 shows the conversions of reactants and the selectivity of C₁ to C₄ products, at 20 bar gauge, a total inlet flow rate of 52.5 mL/min, C₂H₄/H₂ = 0.8 and with the reaction temperature varying from 100 to 250°C (H₂ excess).

The C₂H₄ was completely converted when there was H₂ in the feed gas for all operating temperatures between 100°C and 160°C. As temperature increased above 160°C, C₂H₄ conversion decreased to reach 97% at 250°C. A similar trend in H₂ conversion was observed. This might be caused by acceleration of C₂H₄ adsorption/ desorption with the increase in temperature.

Figure 4A also shows the variation of the ethane selectivity with operating temperature, and it can be seen that the higher the temperature, the lower the ethane selectivity. The dominant reaction at all temperatures is C₂H₄ hydrogenation, as the ethane selectivity is always higher than 94% as shown in Figure 4; however, the ethane selectivity drops with increase in temperature, which implies that the more C₂H₄ is consumed in competing reactions, such as dimerization and hydrocracking.

The selectivity of CH₄ and C₃ and C₄ products (paraffins and olefins) are shown in Figure 4B,C. The selectivity of CH₄ and total C₃ and C₄ products all increased with increasing temperature. As shown in Figure 4, there was an obvious increase in selectivity between 160°C and 180°C. At temperature lower than this critical temperature range, only paraffins were produced and no olefins were formed. At very low temperatures (less than 120°C), the C₂H₄ dimer (butane) had a higher selectivity than either CH₄ or C₃ (odd number hydrocarbons). This indicates that the reaction of C₂H₄ oligomerization was faster than that of hydrogenolysis or demethylation at the low reaction temperatures. When the reaction temperature was increased to 180°C, there was a marked increase in the selectivity of CH₄, total C₃, and total C₄ hydrocarbon products, with CH₄ selectivity increasing the most. The CH₄ selectivity increased from 1.80% to 2.83%, while the total C₃ selectivity only increased from 1.1% to approximately 1.5%; however, the selectivity of C₂H₄ dimer (C₄) was fairly constant (~1.2%) as the temperature was increased from 180°C to 250°C. (See Figure 4.) It is worth noting that the olefin products were only produced when the temperature was higher than 180°C.

The product distribution for the reaction of C₂H₄ in the presence of H₂ appears to occur via reactions that are different from those indicated in the theory on carbon chain growth in FTS. Liu et al.³⁸ suggested two pathways to explain these product distributions. One is the oligomerization (dimerization) of the α-olefins in the feed and the subsequent cracking with H₂ assistance. Another is attributed to the addition of methylene species, which are formed via the demethylation reaction.³⁹ To investigate the different reactions, the yields of CH₄, total C₃, and C₄ products were calculated and the results are shown in Figure 5. In comparison to odd carbon number hydrocarbons, the yield of the C₄ products did not change much with temperatures over the range tested (100°C to 250°C). This suggests that the C₂H₄ dimerization reaction is not sensitive to the reaction temperature. However, for the demethylation products, the yield of CH₄ and C₃ increased more than 20- and 10-fold, respectively. The formation of CH₄ and C₃ can be described by the following two equations:

\[ C₂H₄ + 2H₂ \rightarrow 2CH₄ \]  \hspace{1cm} (A)

\[ 2C₂H₄ + 2H₂ \rightarrow CH₄ + C₃H₈. \]  \hspace{1cm} (B)

Equation (A) represents direct C₂H₄ hydrogenolysis to produced CH₄. Equation (B) shows the methylene species formed by demethylation in carbon chain growth, which produces CH₄ and propene with a mole ratio of CH₄/C₃ equal to 1:1. Equation (B) could be considered an analogical disproportionation. The results in Figure 4 indicate that the CH₄ yield was much higher than that of the C₃ products in the case of H₂ rich feeds. This phenomenon could indicate that a
high coverage of chemisorbed H₂ on the surface of catalysts inhibits the methylene species that take part in chain growth reaction.

3.4.3 Influence of reaction temperature with a H₂ limited feed gas

In another group of experiments, a mixture of C₂H₄/H₂ where C₂H₄:H₂ = 4.8 corresponding a H₂ limited feed gas, was fed to the reactor. The experiments were conducted at 20 bar, a flow rate of 40 mL/min, and the reaction temperature was varied from 100°C to 250°C. Figure 6A shows that the conversion of both H₂ and C₂H₄ were fairly constant at all the
**FIGURE 5** Effect of reaction temperature on CH\(_4\) yield, total C\(_3\) and total C\(_4\), when H\(_2\) is in excess

**FIGURE 6** Effect of temperature on the C\(_2\)H\(_4\) reaction when H\(_2\) is limiting (C\(_2\)H\(_4\)/H\(_2\) = 4.8, total flow rate: 50 mL/min; reaction pressure: 20 bar gauge). A, Conversion of reactants and the selectivity of C\(_2\)H\(_6\). B, Selectivity of CH\(_4\) and C\(_3\). C, Selectivity of C\(_4\)
temperatures. H₂ reacted to completion and the reaction rates of both H₂ and C₂H₄ were essentially the same, which is in agreement with the observed high selectivity of ethane. Thus, even in this H₂ limited situation, the dominant reaction was still C₂H₄ hydrogenation. The experimental results in Figure 6 show that with a H₂ limited feed, the selectivity of ethane decreased from 98% (at 110°C) to 95% (at 250°C). (See Figure 6A.) This suggests that demethylation and oligomerization reactions are more likely to occur at a higher reaction temperature, which is the same as the result obtained for H₂ rich feeds.

For H₂ limited feeds (or correspondingly excess C₂H₄), we see from Figure 6B,C that olefins are the main product, even at a very low temperatures and that the selectivity of C₄ is much higher than that of C₃, which indicates that high partial pressure of C₂H₄ promotes the dimerization reaction. The selectivity of CH₄, C₃H₆ and C₃H₈ all increase with increasing temperature. These results indicate that a high temperature is better for the production of odd carbon number hydrocarbons. However, in comparison to the results of the previous experiment (Figure 4B for a feed with excess H₂), the product distribution of CH₄ and C₃ is different (see Figure 6B.) In this case, the selectivity to C₃ product is higher than that of CH₄ and the selectivity of C₃ increases more rapidly with increasing temperature than the selectivity of CH₄. This indicates that the formation of CH₄ could be limited by the availability of chemisorbed hydrogen. The methylene species formed by demethylation participate in chain growth more easily when C₂H₄ in the feed is in excess, especially at high temperatures. Moreover, the paraffin to olefin ratio decreased with increasing temperature for C₃ also indicating that the availability of H₂ may be limiting.

The change in the selectivity of C₄ products with temperature is shown in Figure 6C and it can be seen that the selectivity of n-butane did not change much with temperature, while the total olefin selectivity increased initially, reached a maximum, and then decreased. The maximum selectivity of cis-2-butene was achieved at about 180°C; for trans-2-butene, the maximum occurred at about 200°C while for 1-butene it occurred at around 220°C. The decrease in the selectivity of C₄ products at a high temperature suggests that the intermediates from C₂H₄ dimerization on the catalyst surface may react to form other hydrocarbons. Similar to the product distribution of propane/propane, the selectivity of butene was significantly higher than butane. The selectivity of both cis-2-butene and trans-2-butene are higher than that of 1-butene.

Figure 7 shows the effect of temperature on the molar formation rate of the C₁, C₃ and C₄ products. These are different from the results seen with excess H₂ in the feed (Figure 5), as the total yield of C₄ product is much higher than that of CH₄ and C₃. This provides strong evidence that chemisorbed H₂ limits C₂H₄ dimerization. In addition, the formation rates of CH₄ and the total C₃ product were different to those found for feeds with excess H₂. At a low temperature (less than 180°C), the mole ratio of CH₄/C₃ was almost 1:1, which corresponds with Equation (B). Under these conditions, some of the C₂H₄ “disproportionates” with H₂ assistance to form a 1:1 mol ratio of CH₄ and C₃ product. At temperature is equal to or above 180°C, the increase in the yield of C₃ is significantly higher than that of CH₄. This finding implies that another reaction occurs to produce C₃. Combined with the decrease in yield of C₄ products, an analogous comproportionation could explain this phenomenon, that is:

\[ C₂H₄ + C₃H₈ \rightarrow 2C₃H₆. \]  \hspace{1cm} (C)

**FIGURE 7** Effect of reaction temperature on the CH₄ yield, total C₃ and total C₄, for a H₂ limited feed.
4 | DISCUSSION

4.1 | Carbon chain growth

Figure 8 shows the product distribution plotted in an ASF plot for light hydrocarbons produced by (a) a feed of syngas, (b) feeds of C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} with excess H\textsubscript{2}, and (c) H\textsubscript{2} limited for different operating temperatures. When the reaction temperature is low, as shown in Figure 8B,C, the online GC cannot detect C\textsubscript{5+} products. However, the product distribution for feeds of C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} is similar to that of normal FTS at reaction temperature higher than 160°C for feeds with H\textsubscript{2} in excess and higher than 200°C, when the feed is H\textsubscript{2} limited. When the carbon number n is greater than 2, the product distribution of light hydrocarbons approaches a straight line, which is consistent with the typical FTS product distribution, as shown in Figure 8A. However, when compared to typical FTS product distribution, several differences can be seen:

**FIGURE 8** Logarithmic product distribution (α-olefins + n-paraffins), as a function of the carbon number (ASF plot). A, Normal FTS feed (H\textsubscript{2}/CO/N\textsubscript{2} = 6:3:1, total flow rate: 30 mL/min; reaction pressure: 20 bar [on gauge]). B, H\textsubscript{2} rich feed (C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} = 0.8, total flow rate: 60 mL/min; reaction pressure: 20 bar [on gauge]). C, H\textsubscript{2} limited feed (C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} = 4.8, total flow rate: 60 mL/min; reaction pressure: 20 bar [on gauge]).
1. Compared to the positive deviation of CH\textsubscript{4} from the ideal ASF distribution in FTS, the CH\textsubscript{4} in the C\textsubscript{2}H\textsubscript{4} hydrogenation reaction product does not deviate from an ASF distribution in a H\textsubscript{2} rich feed (Figure 8B) and even has a negative deviation for H\textsubscript{2} deficient (C\textsubscript{2}H\textsubscript{4} rich) feed (Figure 8C).

2. Due to the dominant reaction of C\textsubscript{2}H\textsubscript{4} hydrogenation, the C\textsubscript{2} product distribution deviated positively from the ideal ASF distribution for n = 2.

3. The C\textsubscript{4} product distribution deviates slightly from the ASF distribution. This can be attributed to C\textsubscript{2}H\textsubscript{4} dimerization, which would enhance C\textsubscript{4} production.

Figure 8 indicates that, in the absence of CO, the reaction of C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2} could also produce the monomers required for chain growth. Moreover, products with both even and odd carbon numbers follow the ASF product distribution. This indicates that the chain growth monomer is not only C\textsubscript{2} and that some adsorbed intermediate CH\textsubscript{x} might be produced by hydrocracking of C\textsubscript{2}H\textsubscript{4}.

Studies are still being done to determine whether the C\textsubscript{2} intermediate formed on the surface of a Co-based catalyst under FT reaction conditions is ethyl, ethyldiene, or vinyl. In addition, it has not been determined whether the carbon chain-growth monomer of the C\textsubscript{1} intermediate is CH\textsubscript{3}, CH\textsubscript{2}, or CH\textsubscript{4} in the FT reaction. However, the large amount of 2-butene obtained from these experiments indicates that adsorbed ethyldiene (CH\textsubscript{3}CH-*) probably formed on the catalyst surface. Kokes\textsuperscript{31} reported that the 2-butene dimer monomer is ethyldiene.

In order to understand the carbon chain growth of C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2} reaction under typical FTS operating conditions, the chain growth probability (α-value) was calculated using Equation 5.

\[
\ln \left( \frac{W_n}{n} \right) = 2\ln(1 - \alpha) + (n - 1)\ln \alpha
\]  \hspace{1cm} (5)

Where: W\textsubscript{n} is the weight fraction of hydrocarbon product containing n atoms; n is the carbon number. The results are summarized in Table 4.

Under conditions of excess H\textsubscript{2} in the feed, the product is almost entirely paraffinic, and as the temperature increases, the α-value decreases. Similarly, the α-value of the total product (including α-olefins and n-paraffins) decreases with increasing temperature for H\textsubscript{2} limited feeds. The trend in the α-value of the individual n-paraffins and α-olefins with temperature is also consistent. This indicates that high temperature is more conducive to the formation of low carbon chain products. In addition, the α-value of the alkane higher for H\textsubscript{2} limited feeds that for feeds with excess H\textsubscript{2}. This indicates that adsorbed H\textsubscript{2} limits the chain growth, as if the chain-growth intermediate is hydrogenated by the surface adsorbed H\textsubscript{2} it forms a paraffin and results in the termination of the carbon chain.

The α-value of total n-paraffins + α-olefins, individual paraffins and olefins under FTS with a syngas feed were calculated and are shown in Table 4. The α-value of total n-paraffins + α-olefins is 0.78, while the α-value of the paraffin is 0.82 and olefins is 0.76. A comparison of α-values of the two feed gases (CO/H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2}) shows that a typical FTS

| Temperature (°C) | α-value | α-olefins + n-paraffins | n-paraffins | α-olefins |
|------------------|---------|------------------------|-------------|----------|
| Feed: H\textsubscript{2}/CO/N\textsubscript{2} = 6:3:1 |
| 200              | 0.78    | 0.82                   | 0.76        |
| Feed: C\textsubscript{2}H\textsubcript{4}/H\textsubscript{2} = 0.8:1 |
| 160              | 0.32    |                        |             |
| 180              | 0.29    |                        |             |
| 220              | 0.27    |                        |             |
| 250              | 0.27    |                        |             |
| Feed: C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} = 4.8:1 |
| 200              | 0.25    | 0.39                   | 0.22        |
| 220              | 0.22    | 0.38                   | 0.17        |
| 250              | 0.2     | 0.35                   | 0.17        |
has a much higher carbon chain growth factor than that of C\textsubscript{2}H\textsubscript{4} hydrogenation. This result indicates that: the either less chain-growth monomer is formed by the reaction of C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2} than the reaction of CO with H\textsubscript{2} or that the monomer is less reactive and that the presence of CO probably has a strong inhibitory effect on hydrogenation of the chain-growth precursor and monomer (chain termination reaction). The CO essentially competes with H\textsubscript{2} for adsorption sites on the catalyst surface; thus, the presence of CO reduces the amount of H\textsubscript{2} adsorbed on the catalyst surface. As this H\textsubscript{2} reacts with chain-growth precursor and monomer (chain termination reaction), it has a significant limiting effect on the chain growth reaction. Based on this idea, the question arises: is it possible to control the $\alpha$-value of the hydrogenation-type chain growth product by controlling the amount of H\textsubscript{2} in the adsorbed state?

### 4.2 Possible C\textsubscript{2}H\textsubscript{4} reactions

When combining our research results with the theories in the literature, the reactions of C\textsubscript{2}H\textsubscript{4} with H\textsubscript{2} could be classified as follows:

1. C\textsubscript{2}H\textsubscript{4} hydrogenation to ethane ($C_2H_4 + H_2 \rightarrow C_2H_6$).
2. C\textsubscript{2}H\textsubscript{4} oligomerization, especially dimerization to C\textsubscript{4} products ($2C_2H_4 \rightarrow C_4H_8$).
3. C\textsubscript{2}H\textsubscript{4} hydrogenolysis to methane ($C_2H_4 + 2H_2 \rightarrow 2CH_4$).
4. Analogical disproportionation ($2C_2H_4 + 2H_2 \rightarrow CH_4 + C_3H_8$).
5. Analogical comproportionation ($C_2H_4 + C_4H_8 \rightarrow 2C_3H_6$).
6. Methylene species formed from C\textsubscript{2}H\textsubscript{4} demethylation participate in carbon chain growth.
7. C\textsubscript{2}H\textsubscript{4} reacts as a monomer in carbon chain growth.

In order to compare the effect of the different experimental conditions on the product distribution, Table 5 lists the product selectivity for C\textsubscript{1} to C\textsubscript{4}. In this study, C\textsubscript{2}H\textsubscript{4} was the sole source of carbon. Thus all products, both odd and even carbon number hydrocarbons, all form from C\textsubscript{2}H\textsubscript{4}, which makes it relatively simple to recognize the possible pathways or secondary reactions of C\textsubscript{2}H\textsubscript{4} in FTS; these reactions may be limited by CO and/or the products of classical FTS; however, these effects do not occur in this study. As the experimental results show, the selectivity of ethane was more than 94% under all the reaction conditions, thus confirming that C\textsubscript{2}H\textsubscript{4} hydrogenation is the dominant reaction.

When C\textsubscript{2}H\textsubscript{4} hydrogenates to produce ethane in FTS, it changes the ratio of paraffin to olefin, but has no direct impact on the chain growth probability. As shown, high reaction temperatures and a high ratio of C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} could inhibit C\textsubscript{2}H\textsubscript{4} hydrogenation to some extent, which may be attributed to activation of the C-C bond at a high temperature. However, this change in the reaction kinetics was small and had no significant effect on the product distribution.

The C\textsubscript{2}H\textsubscript{4} dimerization is a very interesting reaction, since only a small amount of the main dimer (2-butene) is generated when in FTS over a Co catalyst. The generation of 2-olefins is routinely attributed to bond-shift isomerization of the corresponding $\alpha$-olefins in FTS. Based on this theory, it is surmised that 2-$\sigma$-alkyl species generated from partial hydrogenation of $\alpha$-olefins, and then dehydrogenated to form 2-olefins. However, Kokes established a model of C\textsubscript{2}H\textsubscript{4} dimerization based on the results of a study that used hydrogenation of C\textsubscript{2}H\textsubscript{4} over bulk Co. In this model, C\textsubscript{2}H\textsubscript{4} was reversibly bridge adsorbed on the surface of Co, and transformed to the surface intermediate 1,1-$\sigma$-ethylidene with the assistance of the dissociated hydrogen atoms. Two molecules of this intermediate encountered head-to-head to generate cis-2-butene, while 1-butene was produced by a head-to-tail encounter. As C\textsubscript{2}H\textsubscript{4} could react both as an initiator and monomer under FTS conditions, it could be proposed that C\textsubscript{2}H\textsubscript{4} partially hydrogenates to form an ethyl surface species as the chain initiator, and another adsorbed C\textsubscript{2}H\textsubscript{4} inserts to generate 1-butene. In our view, 1-butene might form from both C\textsubscript{2}H\textsubscript{4} direct dimerization and H\textsubscript{2} assistant carbon chain growth. We also believe that these results support that trans-2-butene is a secondary product isomerized by cis-2-butene and that cis-butene, trans-butene, and that 1-butene could be interconverted through internal hydrogen transformation.

C\textsubscript{2}H\textsubscript{4} hydrogenolysis used to form CH\textsubscript{4} is sensitive to reaction temperature and the quantities of chemisorbed hydrogen. Shi and Davis argue that co-fed C\textsubscript{2}H\textsubscript{4} could decrease CH\textsubscript{4} selectivity to some extent. The current experiments show extremely low selectivity to CH\textsubscript{4} for H\textsubscript{2} limited feeds and is in agreement with this conclusion. This might be because C\textsubscript{2}H\textsubscript{4} reacts as a monomer in carbon chain growth rather than producing CH\textsubscript{4} from hydrogenolysis.

C\textsubscript{2}H\textsubscript{4} either reacted directly as a monomer, or demethylased to form methylene, which participated in the chain growth reaction and could be expressed to analogical comproportionation and disproportionation. These reactions
TABLE 5  The selectivity of products C\textsubscript{1} to C\textsubscript{4} on ethylene hydrogenation condition

| Temperature (°C) | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{6} | C\textsubscript{3}H\textsubscript{6} | C\textsubscript{3}H\textsubscript{8} | 1-C\textsubscript{4}H\textsubscript{8} | C\textsubscript{4}H\textsubscript{10} | Trans-2-C\textsubscript{4}H\textsubscript{8} | Cis-2-C\textsubscript{4}H\textsubscript{8} |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Run 5 180        | 0.5%            | 98.98%          | 0%              | 0.17%           | 0%              | 0.35%           | 0%              | 0%              |
| Run 6 110        | 0.92%           | 97.34%          | 0%              | 0.79%           | 0%              | 0.93%           | 0%              | 0%              |
| Run 7 140        | 0.58%           | 95.75%          | 1.01%           | 0.49%           | 0.39%           | 0.30%           | 0.57%           | 0.91%           |
| Run 8 160        | 0.12%           | 96.86%          | 0.34%           | 0.08%           | 0.43%           | 0.18%           | 0.80%           | 1.20%           |
| Run 9 180        | 0.09%           | 96.80%          | 0.29%           | 0.05%           | 0.55%           | 0.16%           | 0.64%           | 1.42%           |
| Run 10 100       | 0.10%           | 99.18%          | 0.00%           | 0.13%           | 0.00%           | 0.60%           | 0.00%           | 0.00%           |
| 110              | 0.12%           | 99.08%          | 0.00%           | 0.15%           | 0.00%           | 0.64%           | 0.00%           | 0.00%           |
| 140              | 0.24%           | 98.79%          | 0.00%           | 0.27%           | 0.00%           | 0.70%           | 0.00%           | 0.00%           |
| 160              | 0.43%           | 98.36%          | 0.00%           | 0.44%           | 0.00%           | 0.76%           | 0.00%           | 0.00%           |
| 180              | 1.80%           | 96.08%          | 0.18%           | 0.91%           | 0.07%           | 0.89%           | 0.06%           | 0.12%           |
| 220              | 2.33%           | 95.35%          | 0.34%           | 0.98%           | 0.12%           | 0.77%           | 0.09%           | 0.20%           |
| 250              | 2.83%           | 94.64%          | 0.36%           | 1.12%           | 0.12%           | 0.81%           | 0.08%           | 0.15%           |
| Run 11 110       | 0.03%           | 98.11%          | 0.07%           | 0.02%           | 0.24%           | 0.14%           | 0.33%           | 1.08%           |
| 140              | 0.05%           | 97.04%          | 0.14%           | 0.03%           | 0.44%           | 0.16%           | 0.63%           | 1.51%           |
| 160              | 0.07%           | 96.41%          | 0.23%           | 0.04%           | 0.59%           | 0.16%           | 0.80%           | 1.69%           |
| 180              | 0.09%           | 96.19%          | 0.34%           | 0.04%           | 0.67%           | 0.15%           | 0.82%           | 1.70%           |
| 200              | 0.15%           | 95.69%          | 0.67%           | 0.08%           | 0.70%           | 0.16%           | 1.07%           | 1.48%           |
| 220              | 0.22%           | 95.29%          | 1.08%           | 0.11%           | 0.78%           | 0.15%           | 1.05%           | 1.33%           |
| 250              | 0.34%           | 95.28%          | 1.59%           | 0.15%           | 0.66%           | 0.16%           | 0.79%           | 1.03%           |

generated odd carbon number products, which affected the product distribution. As the results show, the comproportionation and disproportionation were favored in H\textsubscript{2} limited feeds where there is less dissociated H\textsubscript{2} on the catalyst surface, which is in agreement with the accepted FTS models on Co catalysts. In previous work done by the researchers, Lu et al reported an olefin quasi-equilibrium reaction existed in FTS when using the same catalyst.\textsuperscript{13} This proposed quasi-equilibrium equation is similar to the analogical comproportionation and disproportionation reaction proposed in this work.

In brief, we attempt to isolate the C\textsubscript{2}H\textsubscript{4} reaction system in this work, and find various C\textsubscript{2}H\textsubscript{4} reaction occurs. This is the first step in investigating and understanding the C\textsubscript{2}H\textsubscript{4} reactions in normal FTS. In normal FTS, the strong adsorption of CO on the catalyst surface results in competitive adsorption between CO and olefins (C\textsubscript{2}H\textsubscript{4} in this work). This competition directly suppresses some C\textsubscript{2}H\textsubscript{4} reaction (like dimerization). Moreover, because of the presence of CO, some important phenomenon is easy to be ignored. As we find in this work, in the absence of CO, the ethylene reacted with H\textsubscript{2} to produce products of C\textsubscript{3}, C\textsubscript{5} and C\textsubscript{6}, which fitted the typical FTS product distribution. This phenomenon means FTS-type chain growth is not necessarily only derived from the hydrogenation of CO. The chain growth initiators and monomers required for the FTS reaction can also be formed by olefin hydrocracking, although the chain growth probability in these reactions is much lower than in normal FTS. It may give us a new understanding about the FTS mechanism when viewed from this different angle.

5 | CONCLUSION

With the aim of investigating the feasible reactions paths of C\textsubscript{2}H\textsubscript{4} and their product distribution in FTS, a series of experiments were designed over a Co/TiO\textsubscript{2} catalyst in the absence of CO. When using C\textsubscript{2}H\textsubscript{4}/N\textsubscript{2} as the feed gas, no products could be detected under any of the reaction conditions tested. However, when co-feeding H\textsubscript{2} with C\textsubscript{2}H\textsubscript{4} over a range of
operating temperatures, C2H4 reacted, even at 100°C. Short chain hydrocarbons (including CH4, C3H6, C3H8, 1-C4H8, cis-2-C4H8, trans-2-C4H8, n-C4H10, etc.) were formed.

In the presence of hydrogen, although the dominant product was ethane, varying the temperature and partial pressure of the reactants could lead to the other reaction pathways being enhanced, resulting in varying product selectivity to CH4 and C3,6 olefins and paraffins. C2H4 hydrogenated to form ethane was slightly inhibited by higher reaction temperatures. The main C4 product produced from C2H4/H2 feeds was 2-butene, from C2H4 dimerization. C2H4 hydrogenolysis and demethylation reaction rates were affected by the H2 partial pressure and therefore the quantity of chemisorbed hydrogen. The selectivity of the products of CH4, C3, and C5 with odd carbon numbers increased with increasing temperature. These results indicated that a high temperature preferred the production of odd carbon number hydrocarbons.

In the absence of CO, the products obtained from the C2H4 reacted with H2 fitted a typical ASF product distribution. This indicated that both the chain-growth monomers and initiators were not necessarily only derived from CO hydrogenation, but also from C2H4 reactions. In FTS, C1 normally lay above the ideal ASF distribution, while when using C2H4/H2 feeds, the C1 selectively lay on or even slightly below the ideal ASF plot. The α-values for the C2H4 hydrogenation products was lower (0.32) than that obtained for FTS (0.82) indicating that the rate of termination of the chain growth was higher. Although the feeds used in this work were not the same as that used in normal FTS, the results obtained suggested that C2H4 followed various reaction pathways to form different products, and that it acted as a monomer and as an initiator in the chain growth reactions, thus might affect the product distributions during FTS. These results could have implications for the reaction mechanisms of FTS.

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Yusheng Zhang contributed to Conceptualization-Equal, Data curation-Lead, Formal analysis-Equal, Methodology-Lead, Writing-original draft-Lead. Mgcini Tshwaku contributed to Methodology-Supporting. Yali Yao contributed to Supervision-Equal, Writing-review & editing-Equal. Jianli Chang contributed to Methodology-Supporting. Xiaojun Lu contributed to Writing-review & editing-Supporting. Xinying Liu contributed to Conceptualization-Equal, Supervision-Equal, Writing-review & editing-Equal. Diane Hildebrandt contributed to Supervision-Equal, Writing-review & editing-Equal.

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