SECONDARY REACTIONS OF PRIMARY PRODUCTS OF THE
FISCHER-TROPSCH SYNTHESIS
PART 1. THE ROLE OF ETHENE

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Summary

Co-feeding experiments have shown that ethene readily initiates the
Fischer-Tropsch synthesis without altering the chain-growth probability,
even when it is present in high concentrations. Propagation by ethene was
found to be unlikely.

When present in concentrations of 5 mol% or higher, ethene substan-
tially suppresses methane formation by surface hydrogen and surface inter-
mediate scavenging.

Introduction

It has long been known that small alkenes can act as chain initiators in a
synthesis gas environment [1 - 3]. As early as 1930 it was observed that the
addition of 10 to 30 mol% ethene to the feed led to a substantial increase
in the yield of higher hydrocarbons [4]. Several reviews describe the older
work [5 - 7], but recently a large body of new data has become available.

It has been shown that small alkenes are readily incorporated into the
higher product when co-fed with iron catalysts [8 - 20]. The percentage
incorporation of ethene varies from about 2 to 10%, depending on the
conditions used. Fewer higher hydrocarbons are incorporated: about 1%
propene and even less butene. Similar observations on the incorporation
of small alkenes have been reported with cobalt catalysts [4, 21 - 27],
iron—cobalt [28], ruthenium [29 - 33] and rhodium [34, 35]. Incorporation
is not restricted to small alkenes; it has also been observed with C16-alkenes
[14], ethyne [36], alkanols [9 - 11, 23, 25, 37], cycloalkenes [38 - 40],
benzene [41], ammonia [42, 43] and diethylamine [44].

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Studies involving the co-feeding of $^{14}$C-labelled ethene over cobalt catalysts demonstrated [7, 27] that this alkene acts as an initiator rather than a propagator at concentrations lower than 2 mol%. When co-fed at 5 mol%, ethene also participated in propagation. Other studies [14] showed that most alkenes can act as additional initiators for chain growth, but that alkanes do not participate in any of the reactions. Terminal alkenes incorporated more readily than internal alkenes [29].

In addition to being incorporated, added alkenes can also undergo bond fission. Studies involving the addition of (1-$^{14}$C) n-hexadecane to synthesis gas showed that the $^{14}$C label is observed in the hydrocarbon product obtained [14].

Ekerdt and Bell [33] report that olefin additives with ruthenium catalysts act as scavengers of surface intermediates to form alkylated products. These results are consistent with results by Pichler and Schulz [5] and Emmett and co-workers [9 - 11] on iron and cobalt catalysts. Results obtained by Kobori et al. [31] with ruthenium catalysts and Schulz et al. [14] with iron and cobalt catalysts show that hydrogenolysis and incorporation take place simultaneously and that carbon from the olefins is incorporated randomly in the reaction products, indicating that the scavenger effect of added alkenes [33] can be very small.

In most instances no changes in the rate of methane formation were reported. In a few cases differences were noted, but they seem to depend on the type of catalyst used. With ruthenium a substantial decrease was observed [30]. With iron, the position is not clear. Both increases [17] and decreases [12, 16] have been reported. Sometimes [16] it is not clear whether the lower methane selectivity was due to the dilution by added ethene and its products or was the result of a genuine decrease in the rate of formation. The different reports suggest the operation of different mechanisms. A carbene-olefin mechanism [17] would explain an increase, whereas other mechanisms [13] are more likely to produce a decrease.

These studies show that synthesis products such as terminal alkenes and alkanols can re-adsorb in competition with hydrogen and carbon monoxide, to contribute substantially to the formation of higher products. Arguments for thermodynamic equilibrium [45] and experimental evidence [22, 46] have shown that terminal alkenes are the primary synthesis products. At elevated pressures or with catalysts that favour the adsorption of molecular carbon monoxide, oxygenates are additional primary products [20]. Alkanes and internal alkenes are secondary synthesis products arising from initially formed terminal alkenes [22, 46]. It has been suggested that methanation proceeds via the hydrogenation of surface carbon [47]. Secondary reactions of the initial synthesis products during the synthesis process may have a strong influence on the overall product distribution and be an important route. Model studies [48] and experimental evidence with cobalt [26], ruthenium [30] and iron [12, 13] catalysts have shown that this route can result in a higher chain-growth probability for $C_{24}$ chains than for $C_1$. 
Many of the available literature data have been acquired under atmospheric pressure. However, synthesis pressure is known [14] to have a considerable influence on the secondary reactions for iron catalysts under conditions similar to those prevailing in industry. Particular attention has been given to methane selectivity, olefin selectivity and overall synthesis activity. This communication reports on the role of ethene.

Experimental

Two catalysts were used in this study, both prepared by partial combustion of iron citrate complexes [49]. One catalyst, A, contained only iron and the other, B, consisted of iron and calcium in equiatomic amounts. The catalyst precursors were crushed and screened to particle sizes in the range of 0.2 to 0.6 mm and reduced at a pressure of 300 kPa hydrogen at a flow rate of $1.6 \times 10^{-6} \text{ m}^3 \text{s}^{-1}$ for 3 to 5 h at 433 K, and subsequently for 16 to 20 h at 573 K.

The catalytic behaviour of the materials was evaluated in a fixed-bed microreactor system [50] based on the concentric tube design [51]. The product was analysed by means of an on-line gas chromatographic data system [52-54]. The reaction conditions employed were a pressure of 2.0 MPa, a temperature of 543 K and a flow (VHSV = 1000) of synthesis gas with a mol ratio of $\text{H}_2:\text{CO} = 0.5$.

Synthesis gas containing ethene (5 or 10 mol%) was prepared in and fed from a gas-mixing station [55]. Flow control was achieved by means of Brooks mass flow controllers.

Synthesis experiments were always started with pure synthesis gas only. When steady-state conditions had been reached, the pressure was lowered to 0.1 MPa and immediately raised to the working pressure of 2.0 MPa using ethene-containing synthesis gas. Use of this procedure permitted rapid replacement of the pure synthesis gas with that in which ethene was present. Before termination of experiments the reverse procedure was followed, in order to ascertain whether any observed changes in the catalytic behaviour under ethene co-feeding conditions were reversible.

Results

In presenting the results, use is made of relative units of activity and selectivity, the base data relating to experiments in which no co-feed was used. The results presented have been calculated on the assumption, as made by others [30], that the rate of $\text{C}_2$ production under conditions when co-feed was used was equal to that observed under normal conditions. Steady state conditions were reached after about 100 ks on stream. The product distributions before and after co-feeding were identical.

Ethene was co-fed at concentrations of 5 and 10 mol% over catalyst A and at 10 mol% over catalyst B. The rate of hydrocarbon synthesis,
expressed as the conversion of single carbon units in the carbon-monoxide-plus-ethene pool to hydrocarbons, virtually doubled in all cases (Fig. 1). When co-fed at a concentration of 10 mol% with catalyst A, up to 26% of the added ethene was converted to higher hydrocarbons. With catalyst B, the corresponding value was 68%. Co-feeding at a concentration of 5 mol% with catalyst A resulted in 66% incorporation.

Conversion of carbon monoxide to hydrocarbons (before and after co-feeding) was 10% with catalyst A and 25% with catalyst B.

The olefin selectivity, expressed as the mass percentage alkenes in the C₂ to C₅ hydrocarbon product fraction (corrected for unconverted ethene and ethane formed by hydrogenation of the co-fed ethene), increased significantly in all cases (Fig. 2).

Earlier we reported in a preliminary note [12] that the co-feeding of ethene in the case of an iron-calcium catalyst resulted in a substantial suppression of the methane selectivity (to ca. 25% of the normal value) and a reduction in the rate of methane formation (to ca. 50% of the normal value). We have now found that similar results are obtained with catalyst A and with other iron-based catalysts.

No change (other than that of a transitory nature) was observed in the chain-growth probability and all changes observed in the catalytic behaviour under co-feeding conditions could be reversed, by terminating the supply of co-feed.

Experiments in which ethene and hydrogen alone were fed resulted in a product stream consisting of hydrogen, ethene and ethane only.
Fig. 2. Influence of ethene addition on the olefin selectivity, expressed as the mass percentage alkenes in the C₂-C₅ hydrocarbon product fraction (corrected for unconverted ethene and ethane formed by hydrogenation of the co-fed ethene).

**Discussion**

**Transient behaviour**

When the feed was changed from pure synthesis gas to ethene-containing synthesis gas, a temporary drop in the synthesis activity (Fig. 1) and chain-growth probability was observed. The decrease is attributed to a momentary disturbance of the steady-state situation. The disturbance disrupts hydrocarbon synthesis and only the short-chain hydrocarbon entities formed on the surface before the disturbance report in the product, as evidenced by the lower growth probability observed.

Apparently hydrocarbon synthesis is soon resumed, as indicated by the increase in activity and growth probability. Both parameters increase sharply at first and then rise more slowly to reach steady state after a relative time (i.e. relative to the moment of feed change) of about 100 ks, at which time the activity is much higher than that found before ethene was co-fed.

We attribute this observed behaviour to the high reactivity of ethene. The temporary suppression of the adsorption of synthesis gas is caused by the sudden adsorption of large amounts of ethene. Immediately thereafter the adsorbed ethene incorporates readily, synthesis gas adsorption equilibrium is restored, and a sudden increase in both activity and growth probability results. A steady-state situation is then slowly reached. A full explanation for the comparatively long period required to reach steady state is still being sought.

**Relative rate of ethene incorporation**

In line with the considerable body of literature on the subject, an increase in the rate of hydrocarbon synthesis was observed. Regardless of
the catalyst, the co-feed concentration or the conversion level, the rate of hydrocarbon synthesis doubled. Up to 66% of the added ethene was found to be converted to higher hydrocarbons. This finding is in contrast to reports in the literature, which indicate that about 10% is the upper limit of ethene incorporation with iron catalysts. In most cases the co-fed concentration was about 1 to 3% and/or the synthesis reaction was carried out at atmospheric pressure. Such studies, as well as those [16] conducted at higher pressures (2 MPa) and higher co-feed concentrations (20%), indicate that about 2 mol ethene incorporate per 100 mol converted CO (to hydrocarbons). In the present case, the incorporation per 100 mol converted CO is 40 to 50 mol ethene, whatever the co-feed concentration or the catalyst used. The only differences between the present study and those reported earlier are the lower $H_2:CO$ ratio used in the feed, and the method of catalyst preparation.

**Participation of ethene in hydrocarbon synthesis**

Literature data [7, 27] involving tracer experiments with cobalt catalysts indicate that ethene acts as an initiator rather than a propagator when used at concentrations below 2 mol%. At concentrations of 5 mol% and higher, propagation also occurs. However, similar experiments [16] with iron catalysts indicate initiation only.

Large-scale propagation by ethene is unlikely. If this were the case, a concentration-dependent rate of incorporation and an increase in the value of the chain-growth probability would be expected. Neither is observed. For the same reason it is unlikely that the scavenger concept, as introduced by Ekerdt and Bell [33], applies in the present case.

There could be another explanation, as a result of the formation of intermediates during ethene hydrogenolysis. In addition to its role as a chain initiator, ethene could decompose into reactive intermediates which might contribute to chain growth at all growth points. In this case the value of the growth probability would not be affected by the presence of co-feed and ethene fragments would be evenly distributed among the various products. However, it is felt that this type of process is not likely to be occurring in the situation under discussion. Large-scale hydrogenolysis of ethene has been reported by Barrault *et al.* [17], but for operation at much higher temperatures (ca. 200 K higher). Tracer studies [14] conducted under conditions similar to those used in the present study have shown that only 0.1% of the ethene undergoes hydrogenolysis to methane. Moreover, the unlikelihood of ethene hydrogenolysis is evidenced by observations that a product consisting of hydrogen, ethene and ethane results only from the reaction of ethene with hydrogen.

Large-scale initiation seems to be much more likely. We have shown that one molecule of ethene and two molecules of carbon monoxide are simultaneously converted to (other) hydrocarbons. We note that in our experiments the probability of propagation, $P$, has a value of 0.72 under steady-state conditions. The average number of carbon atoms per molecule...
of product is therefore \((1 - P)^{-1} = 3.57\). This value is consistent with the average value of 4.00, which would result from initiation by ethene.

**Repression of methane**

In contrast to the large volume of reports indicating no influence of the co-feed on the rate of methane formation and the report showing an increase with iron catalysts [17], we observed a substantial decrease, which is in agreement with observations involving ruthenium catalysts [30]. The extent of the decrease depended on the co-feed concentration and the catalyst used. In principle, the decrease in methane concentration could be explained by any one or a combination of four different effects:

(i) secondary reaction of methane with ethene;

(ii) an unchanged rate of methane production with a superimposition of the results of a large-scale participation by ethene in the synthesis reaction, whereby the methane concentration decreases at the percentage level, although the rate of methane formation remains constant;

(iii) inhibition of methane formation by the presence of adsorbed ethene; and

(iv) large-scale participation of ethene in the hydrocarbon synthesis through reaction with single-carbon intermediates which are also responsible for methane formation, thereby reducing the surface concentration of these intermediates and hence the rate of methane formation.

The highly unlikely occurrence of effect (i) was discounted from the results of a simple experiment. The addition of an equimolar stream of methane to the ethene stream did not result in a significant decrease in the ethene concentration, neither was a significant increase in synthesis activity observed.

The occurrence of effect (ii) can also be easily discounted. Since the rate of methane formation remains unaffected by ethene addition, co-feeding will result in a dilution of the product obtained under standard conditions by the products derived from the added ethene. Thus the methane selectivity should have a value of ca. 50% in all three cases. However, a significantly lower value in each case is found [12], indicating a decrease in the rate of methane formation.

Effect (iii) is much more likely to occur. If ethene is adsorbed in large amounts under synthesis conditions, it will act as a surface-hydrogen scavenger, as reflected in the observation that 60% of the C2 species in our reaction product were hydrogenated. A decrease in the concentration of surface hydrogen will affect the product distribution.

If we accept a simple chain-growth mechanism as proposed by Kugler [56], then hydrocarbon synthesis is initiated by the formation of an activated single carbon intermediate as shown in Fig. 3. This intermediate either follows Anderson–Schulz–Flory polymerization kinetics or undergoes a hydrogenation step to produce methane. Under conditions that limit the availability of active surface hydrogen [56], there is a decrease in the rate of formation of methane. Since the desorption of C2+ hydrocarbons as
alkenes does not require the participation of active hydrogen, the rate of formation of higher hydrocarbons need not be affected. We suggest that a similar effect is in operation in the present case, where a ca. 50% decrease in the rate of methane formation is observed.

A contribution from effect (iv) cannot be excluded. Large-scale synthesis initiation by ethene is likely to affect the formation of methane. Following Kugler [56], we believe that, under synthesis conditions without co-feed, the single carbon intermediate in the synthesis reaction scheme presented in Fig. 3 can (a) undergo hydrogenation to form methane, (b) initiate hydrocarbon synthesis, or (c) propagate synthesis by reacting with either adsorbed ethene, growing hydrocarbon chains or itself. If ethene is present in large amounts, its reaction with the intermediate will largely suppress any of the other reactions involving the intermediate, including methane formation.

In conclusion, both hydrogen scavenging and intermediate scavenging by ethene are thought to be responsible for the suppression of methane formation.

**Olefin selectivity**

Additional support for the theory of hydrogen scavenging by ethene is provided by the substantial increase in the olefinic content of the product shown in Fig. 2 (after correction for unconverted ethene and ethene converted to ethane). The increase was dependent on the catalyst used and the co-feed concentration, as can be expected when hydrogen scavenging occurs.

In contrast to the transient changes in the synthesis activity and growth probability, the olefin selectivity increases immediately. This observation also reinforces the scavenger role of ethene.
Implications for the mechanism of hydrocarbon synthesis

An important observation was that the value for the probability of chain growth was not affected by the co-feed. This indicates that the process of propagation is largely unaffected by the co-feed — it continues in the same way regardless of the type of initiator used (Fig. 3). As a consequence of the rapid propagation of ethene, secondary reactions involving initiation by the primary product ethene are likely to occur. Such reactions may explain why C_2 products often have a relatively low concentration in Anderson–Schulz–Flory plots.

Conclusions

The results obtained from this study show that ethene can initiate the Fischer–Tropsch synthesis. When present in high concentrations, it can act as an initiator for the entire higher hydrocarbon product. Initiation by ethene is so rapid that it can be expected that, under normal synthesis conditions, a substantial fraction of the primary product ethene will re-adsorb and initiate secondary chain growth, as reflected in the generally low relative yield of C_2 products in the final product mixture.

It is, however, unlikely that ethene also propagates the synthesis reaction or acts as a scavenger of surface intermediates larger than C_1 species. Except for the methane yield, the product distribution is not affected when ethene initiates synthesis. Methane formation is substantially suppressed when ethene is present in large amounts. The suppression is attributed to large-scale scavenging of surface hydrogen and C_1 intermediates (some of which are methane precursors).

No evidence of bond fission is observed and it is unlikely that the carbene–olefin mechanism is applicable to the present case. This study contains insufficient data to allow any conclusion about the particular synthesis mechanism involved. Future studies should enable a more detailed picture of the hydrocarbon synthesis to be built up.

References