FISCHER–TROPSCH SYNTHESIS ON IRON-BASED CATALYSTS: THE EFFECT OF CO-FEEDING SMALL OXYGENATES

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Summary

Co-feeding experiments have shown that ethers can participate substantially in the Fischer–Tropsch synthesis with iron catalysts. Dimethyl ether is thought to be capable of building up surface complexes which are very similar to those naturally occurring during synthesis. Diethyl ether undergoes rapid reaction, probably deoxygenation to ethene, which in turn initiates hydrocarbon synthesis.

The results show that important similarities exist in the nature of the hydrocarbon synthesis in the Fischer–Tropsch and methanol-to-gasoline processes.

While ethers are similar to naturally occurring synthesis intermediates, aldehydes are quite different and their presence suppresses and entirely changes normal synthesis behaviour. The results underline the important role that oxygenates can play in hydrocarbon synthesis on iron catalysts.

Introduction

One of the most severe limitations of the Fischer–Tropsch (FT) process is its poor selectivity. When the synthesis is geared to gasoline production, a very broad product spectrum is obtained. Because the hydrocarbons are characteristically linear, a low octane gasoline results. This disadvantage is not shared by the methanol-to-gasoline (MTG) process [1], which produces high octane gasoline selectively from methanol.

It is known that the primary products in FT synthesis are lower olefins [2, 3]. Secondary reactions of the initial products during the synthesis process have an important influence on the overall product distribution. It has long been known that small alkenes can act as chain initiators in a synthesis gas environment [4-6]. As early as 1930 it was observed that addition of 10 to 30 mol% propene to the feed led to a substantial increase
in the yield of higher hydrocarbons [7]. Several reviews describe the older work [8 - 10], but recently a large body of new data has become available. Elsewhere [11] we have given an overview of the relevant literature.

We have studied the occurrence of secondary reactions of ethene [8], propene [12] and butene [13]. Although differing in reactivity, each of these alkenes was found to be capable of re-participation in the synthesis reaction by initiating secondary chain growth. The reactivity in this reaction was found to increase in the order propene < butene < ethene.

Similar to the FT process the MTG process starts essentially with synthesis gas, from which methanol is produced. In the second stage of the process, methanol is dehydrated to dimethyl ether (DME), which in turn reacts to form lower olefins [14], which are identical to the primary FT product. The olefins subsequently react to form hydrocarbons in the gasoline range [15, 16]. Because of the similarity in primary products and the large difference in selectivity of the final product spectrum, a study of the secondary reactions of the two forms of synthesis may contribute to an improved understanding of the nature of the selectivities involved.

Secondary reactions in FT synthesis are not restricted to small alkenes, incorporation has also been observed with a variety of different compounds [17]. One group of these, alkanols, are important products with iron catalysts, and have received relatively much attention. Tracer studies involving iron catalysts showed that complexes resembling adsorbed alkanols are formed during synthesis and act as intermediates in the building of higher hydrocarbons [18 - 20]. Similar observations were made with cobalt catalysts [21 - 23]. However, alkanols are certainly not the only important primary or intermediate oxygenate products, although they seem to have been singled out for co-feeding studies.

Because DME is able to form the same lower olefins in the MTG process as those found as the primary product of the FT synthesis, we have studied the role of DME and some other small oxygenates in both forms of synthesis. The results of these studies indicate that these reaction can give important information on probable reaction routes. We address the effect of co-feeding small oxygenates to the FT synthesis in this communication.

Experimental

The catalyst used in this study was prepared by partial combustion of iron citrate complexes [24]. The oxidic catalyst precursor was crushed and screened to particle sizes in the range of 2 to 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 - 5 h at 433 K and subsequently for 16 - 20 h at 573 K.

The catalytic behaviour was evaluated in a fixed bed microreactor system [25] based on the concentric tube design [26]. The product was analyzed by means of an on-line gas chromatographic data system [27 - 29]. 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 H₂:CO = 0.5. Synthesis gas containing oxygenates was prepared in and fed from a gas mixing-feeding station [30].

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

Results and discussion

In presenting the results, use is made of relative units of activity and selectivity, the base data relating to control experiments in which no co-feed was used. In view of the highly exothermic reaction, temperature digressions can easily occur when oxygenate-containing feed is pressurized into the reactor, resulting in biased activity data. Control experiments have shown that the system remained isothermal during the drastic lowering and raising of pressure. This point is an important feature of the design of the reactor used [26].

The reproducibility was in all cases better than 2%, showing that the experimental technique used in this study is capable of providing sufficiently meaningful kinetic data for our purpose.

The results presented have been calculated on the assumption, which is similar to that made by others [31], that the rate of oxygenate production under conditions when co-feed was used, was equal to that observed under normal conditions.

Synthesis activity is expressed as the conversion of single carbon units in the carbon-monoxide-plus-oxygenates pool to hydrocarbons. Methane selectivity is expressed as the mass percentage of methane in the product (corrected for unconverted oxygenates). Olefin selectivity is expressed as the mass percentage of alkenes in the C₂ - C₅ hydrocarbon fraction (corrected for unconverted oxygenates and oxygenates formed by hydrogenation of co-fed oxygenates.

Steady state conditions were reached after about 100 ks on stream. The product distributions before and after co-feeding were identical.

Conversion of carbon monoxide to hydrocarbons (before and after co-feeding) was approximately 10%. The rate of hydrocarbon synthesis was ca. 7 μmol s⁻¹ g cat⁻¹.

Dimethyl ether

Co-fed at a 10 mol% concentration, dimethyl ether (DME) caused an initial decrease in the overall catalytic activity, similar to that observed with
other co-feeds [11-13], whilst a temporary increase in olefin selectivity was observed (Fig. 1). After the temporary change, an olefin selectivity was maintained which was similar to that obtained in the control experiments. In contrast to the essentially unaffected olefin selectivity, the activity was 28% higher than that obtained without co-feed, indicating incorporation of DME. The methane selectivity exhibited a decrease of 23% relative to that obtained without co-feed. If it is assumed that DME is not converted to methane, then the decrease in methane selectivity is entirely explained in terms of dilution.

Anderson-Schulz-Flory (ASF) statistics are followed throughout, indicating that DME is incorporated into the growing chains and not
converted to a specific hydrocarbon. The growth probability, $P$, first exhibits a decrease, similar to that observed immediately after adding small alkenes to the feed \([11 - 13]\), after which it is maintained at a level slightly higher than that obtained in the control experiments. The change in the value of $P$ is so small that no significant change in the hydrocarbon synthesis mechanism is likely to have occurred on DME incorporation.

It could be argued that DME induces restructuring of the surface. Although an increased surface area could explain the increase in overall activity, it is very likely that the synthesis characteristics of the catalyst (e.g. the value of $P$) will change during a DME-induced restructuring of the surface. The results show that this is not the case. Selectivity changes are observed when co-feeding DME which are similar to those observed when ethene was co-fed, suggesting direct participation of DME in the hydrocarbon synthesis.

In line with reports on alkanols \([18 - 20]\), we therefore suggest that DME forms a surface complex during synthesis on iron catalysts which acts as an intermediate in the hydrocarbon synthesis. The build up of the complex is relatively slow, steady state being reached only after 40 ks. During the transition period, synthesis activity is suppressed, indicating that many synthesis sites are covered by surface complexes which are not active in the synthesis. Therefore DME as such is not active in the synthesis but can be slowly converted into active intermediate complexes. Furthermore, as noted with small alkene addition, all observed changes in the catalytic behaviour were reversible. We therefore conclude that the intermediate complexes are not dissimilar to those normally playing a role in the hydrocarbon synthesis.

It could be speculated that the intermediate complexes can be regarded as a link between the hydrocarbon synthesis as occurring in the FT process and the synthesis by means of MTG process.

**Diethyl ether**

Because of its vapour pressure, the maximum attainable concentration of diethyl ether (DEE) under our experimental conditions is 3.3 mol%, which is the percentage used in this study.

In contrast to the catalytic behaviour observed when co-feeding DME, no dip was observed in the activity behaviour, and both the olefin selectivity and activity increased immediately, reached a maximum level and then slowly decreased again to maintain almost steady values (Fig. 2). The absence of a dip and the immediate increase in activity indicate that no large scale build-up of surface complexes is involved, but rather an immediate reaction of DEE.

When the co-feeding was terminated, both the olefin selectivity and the activity decreased relatively slowly to reach the level obtained before co-feeding. This is in contrast to the immediate reversion to the original values observed with all the other co-feeds used, and could indicate that a relatively stable intermediate surface complex is involved. In view of the
above discussion it seems therefore likely that only few such complexes are involved, but that their reactivity is high.

The methane selectivity decreased to reach a minimum value, which is one-quarter of the value observed in the control experiments. The minimum is reached 30 ks after co-feeding commenced. This time coincides with the maximum in the activity, the value of which is then four times the normal value. The decrease in methane selectivity is therefore ascribed to dilution, assuming that DEE is not converted to methane.

With the exception of C₄ hydrocarbons, ASF statistics are maintained throughout, without any change in the value of P. The concentration of C₄ is much larger than would be expected from predictions based on ASF statistics. Analysis of the results revealed that the butane concentration
did not differ from that obtained from experiments without co-feed and that the increase in C4 hydrocarbons was solely due to an increase in butene production.

In order to ascertain whether DEE is incorporated into the growing hydrocarbon chains in addition to being converted to butene, the concentration of butene which is in excess of that predicted by ASF statistics, is calculated and from that its additional rate of formation, \( \Delta r_{C4} \), determined. This rate is compared (Fig. 3) with the additional rate of total hydrocarbon synthesis (including the extra butene and relative to that obtained in experiments without co-feed), \( \Delta r_{HC} \), and the difference between the two rates. The latter, \( \Delta r_{INC} \), is the rate of additional hydrocarbon synthesis via incorporation.

![Fig. 3. Comparison of the rates of formation of excess butene (\( \Delta r_{C4} \)), of additional hydrocarbons in general (\( \Delta r_{HC} \)) and of additional hydrocarbons via incorporation (\( \Delta r_{INC} \)).](image)

It is clear from Fig. 3 that DEE is mainly converted into butene but is, to a lesser extent, also incorporated in the main synthesis reaction. One possible explanation is that DEE is dehydrated to ethene. This alkene is then subsequently dimerized to butene or incorporated into the growing hydrocarbon chains as discussed elsewhere [11].

It could be argued that, by analogy, DME should then form ethene, and no increase in the concentration of this alkene was observed when DME was used as a co-feed. However, if additional ethene was formed, it would not necessarily increase its product concentration since it has been shown that ethene is readily incorporated. Incorporation of butene is less rapid than is
the case with ethene, and hence its product concentration is increased. Therefore, dehydration of the ethers and subsequent dimerization of the ensuing alkenes under synthesis conditions is quite plausible.

No poisoning effects are noticed with the ether additions. Furthermore, all observed changes in catalytic behaviour were reversible. We therefore conclude that all reaction intermediates involved are natural to the hydrocarbon synthesis.

**Acetaldehyde**

Because of its vapour pressure, the maximum attainable concentration of acetaldehyde is 3 mol%, which is the percentage used in this study.

In the presence of acetaldehyde an entirely different product spectrum is observed, consisting of almost equal amounts of hydrocarbons and oxygenates (Fig. 4). Neither the hydrocarbons nor the oxygenates follow an ASF distribution. Oxygenates with an odd carbon number have the same (low) concentration, while the even carbon numbers (mainly aldehydes) are associated with much higher concentrations, suggesting a C₂ growth.

![Fig. 4. Typical product spectrum observed 80 ks after DEE co-feeding commenced; (○) hydrocarbons (C₁ units), (Δ) oxygenates (C₂ units).](image-url)
The odd C number oxygenates could be hydrogenolysis products of the even ones. In the case of hydrogenolysis, additional methane is likely to be formed and the methane yield is far in excess of that predicted by ASF statistics.

If it is assumed that excess methane (in excess of ASF) is a hydrogenolysis product of oxygenates and all oxygenate products are formed from acetaldehyde only, then the number of carbon and oxygen atoms in the feed should be balanced by those in the product. A C-balance of 97.0% and an O-balance of >92% were found, supporting this assumption. If it is further assumed that all hydrocarbons except excess methane are formed from CO only, then again a mass balance should support the assumption. Indeed, the C-balance was found to be 99.3% and the O-balance 99.5%. It therefore seems likely that hydrocarbons are formed from CO and oxygenated products from acetaldehyde.

The conversion of CO to hydrocarbons decreased from 12 to 6% when acetaldehyde was co-fed, indicating a suppression of hydrocarbon synthesis from CO by 50%. That acetaldehyde indeed suppresses synthesis was shown in another experiment, where the co-feed was introduced by a high pressure liquid pump. The lowest attainable concentration was 50 mol%, and at this concentration no hydrocarbon synthesis was observed.

At the concentration of 3 mol%, practically all acetaldehyde reacted and the conversion of the mixed feed to hydrocarbons and oxygenates was also 12% on a molar basis. That no change is observed in the overall conversion level indicates that the same number of sites is involved for the different reactions. However, the hydrocarbon synthesis mechanism has changed, since the hydrocarbon product distribution no longer follows ASF statistics (Fig. 5). We suggest that the presence of a high concentration of oxygenates on the surface affects the chain growth probability, making it

![Fig. 5. Typical hydrocarbon ASF plot of the product observed 80 ks after DEE co-feeding commenced.](image-url)
a function of the adsorbed species. There is some analogy between the hydrocarbon product spectrum and that of the oxygenates (Fig. 4).

While ethers are similar to naturally occurring synthesis intermediates, acetaldehyde is quite different and its presence suppresses and entirely changes normal synthesis behaviour, regardless of the exact nature of its influence.

Acetaldehyde is extremely reactive under synthesis conditions. Oligomerization (most probably condensation reactions) plays a major role in product formation, while the production of methanol is also substantial. The latter observation, in addition to the result of the mass balances and the distribution of oxygenates with an odd carbon number, strongly suggests the occurrence of substantial hydrogenolysis.

**Hydrocarbon synthesis**

The observed results suggest that ethers are similar to naturally occurring synthesis intermediates, while acetaldehyde is not. This observation indicates the nature of the carbon–oxygen bonding in the synthesis intermediates.

The fact that DME readily participates in both the FT and the MTG type synthesis suggests that the two types of synthesis are not unrelated. It could be speculated that intermediate complexes can be regarded as a link between hydrocarbon synthesis as occurring in the FT process and synthesis by means of the MTG process.

**Conclusions**

Dimethyl ether, when present on iron surfaces during hydrocarbon synthesis, slowly builds up surface complexes which are probably very similar to those occurring naturally during synthesis. Therefore addition of this ether leads to enhanced synthesis activity without affecting the catalytic behaviour. The results indicate the existence of important similarities in the nature of hydrocarbon synthesis in the FT and MTG processes.

In contrast, diethyl ether undergoes rapid reaction, probably deoxygenation to ethene, which in turn initiates hydrocarbon synthesis.

While ethers are similar to naturally occurring synthesis intermediates, aldehydes are quite different, and their presence suppresses and entirely changes normal synthesis behaviour, regardless the exact nature of their influence.

We therefore agree with several reports in the literature stressing that oxygenates can play a very important role in hydrocarbon synthesis on iron catalysts.

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