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Use of probe molecules for Fischer–Tropsch mechanistic investigations: A short review

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ABSTRACT

The Fischer–Tropsch synthesis (FTS) mechanism is still not fully understood and the product distribution does not generally follow a typical Anderson–Schulz–Flory (ASF) distribution. In order to improve the understanding of the reaction mechanism and in an attempt to explain the deviations observed from the ASF distribution, additives such as olefins, alcohols, carbon dioxide, water, and isotope markers, have been used in the FTS. This paper briefly reviews the effect of additives and their impact on the FTS mechanism.

1. Introduction

Fischer Tropsch synthesis (FTS) is the process for converting synthesis gas (syngas), a mixture of carbon monoxide (CO) and hydrogen (H_2) to hydrocarbons. It is used for the production of synthetic fuels and other waxy products from feedstocks such as natural gas, coal and biomass. In short, any carbon containing compound can be converted through a combination of gasification, reforming or partial oxidation and FTS to a mixture of hydrocarbons from the simplest hydrocarbon (methane) to much longer molecules (C_{60+}). The equation below (Eq. (1)) shows the reactions for syngas to paraffinic hydrocarbons. Other products, such as oxygenates and olefins, may also be formed. The product distribution of the FTS is dependent on a number of factors including the type of catalyst used, ratio of hydrogen to carbon monoxide in the syngas, temperature, pressure and additives or impurities in the syngas. Despite numerous studies over several decades, the mechanism of the FTS still remains controversial. The methylene (CH_2) insertion mechanism is currently the most widely accepted primary mechanism, supported by the vast majority of studies [1–5]. It involves: (1) CO adsorption and dissociation to adsorbed C and O atoms, (2) hydrogenation of C atoms to CH_x species, and (3) chain growth by insertion of CH_x monomers into the metal–carbon bond of the adsorbed alkyl chain. Chain termination (4) can lead to the formation of olefins and paraffins.

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O \qquad (1)$$

The formation of hydrocarbons through a stepwise insertion or addition of CH_x intermediates with constant chain growth probability (α) should result in an ideal Anderson–Schulz–Flory (ASF) distribution, as described by Eq. (2), where w_n is the weight fraction of the species with carbon number n, and α is the chain growth probability, assumed to be independent of n. However, for most catalysts, including the most commonly used iron and cobalt catalysts, clear deviations from this ideal distribution are generally observed.

$$w_n = n(1-\alpha)^2 \cdot \alpha^{n-1} \qquad (2)$$

This paper reviews the hypotheses formulated by various researchers on the ASF distribution of FTS products, which include secondary reactions such as α-olefins re-adsorption followed by their initiation of new hydrocarbon chains (Section 2) or the superposition of two different chain growth mechanisms with different ASF distributions (Section 3). The formation of by-products such as water and carbon dioxide will also be reviewed (Section 4).

The nature of the catalyst, its support, and the use of promoters, all have an influence on the FTS mechanism and the product distribution. Although the nature and characteristics of the catalysts involved in the different mechanistic steps are still a point of conjecture and full characterisation is lacking in the literature, hypotheses based on the activity of the active sites have been postulated to explain the observed deviations from the ideal ASF distribution.

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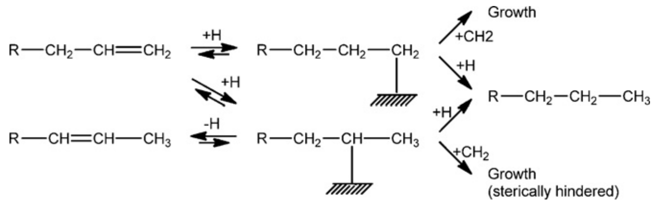

Fig. 1. Secondary olefin reaction in the FTS [9].

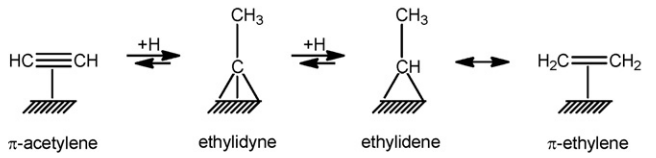

Fig. 2. Possible surface mechanism for surface conversion of acetylene and ethylene [36,37].

Madon and Taylor interpreted the deviation from the ASF distribution to be due to differences in the structure of active sites causing variation in the growth probability [6]. Some authors also suggested that while some catalytic sites are able to promote both hydrogenation of adsorbed intermediates (secondary hydrogenation) and chain growth to high molecular weight products, other catalytic sites do not promote chain growth, but hydrogenation only [7]. According to this theory, a higher termination rate could be observed on the sites that promote only hydrogenation, generating lower molecular weight product. However, catalysts and their characteristics will not be included in this review. Instead this review will focus on the effects of syngas additives on the chain growth process and mechanism.

Over the last three decades, numerous studies using probe molecules such as light olefines, alcohols, water, carbon dioxide, and isotope tracers, added to the syngas, have been carried out in an attempt to develop hypotheses for the mechanism of the FTS, and to explain the deviations from the ideal ASF distribution. This will be reviewed in the following sections.

2. Olefin re-adsorption – use of unsaturated hydrocarbons as probe molecules

For products obtained using cobalt catalysts, deviations from the typical ASF distribution are traced back by many authors to re-adsorption and incorporation of olefins followed by subsequent chain growth (secondary chain propagation) (Fig. 1) [7–9].

Diffusion limitations within the liquid-filled catalyst pores slow down the removal of increasing chain length 1-alkenes, increasing their residence time, and therefore the probability of re-adsorption and subsequent chain initiation and growth [10]. In the olefin re-adsorption model, α is therefore a function of the carbon number n [2]. For Co catalysts, 1-alkene re-adsorption in essence promotes hydrogenation (paraffin formation, 70%), and chain growth (higher hydrocarbons, 30%). Formation of oxygenates represents only a small fraction (4%) of the process [11].

C_1 and C_2 products formed during the FTS do not generally follow the same ASF distribution as C_{3+} products, and it is speculated that the ethylene formed by CO hydrogenation has a higher tendency to re-adsorb and re-enter the chain growth process [12] via the methylene insertion mechanism [1]. Ethylene has therefore been widely used as a probe molecule (co-fed with syngas) to investigate its influence on the FTS mechanism [8,12–25].

All studies have shown that ethylene acts primarily as a chain initiator. In addition, some authors have speculated that ethylene can also be dissociated to C_1 intermediate fragments by hydrogenolysis to serve as a source of monomer for chain growth [12,18,20]. While the same authors found no evidence that ethylene itself does not participate in the propagation of hydrocarbon chains [12,20], Schulz claimed that it can, to some extent, act as a C_2 monomer for chain growth [26].

Methane formation is substantially suppressed for high ethylene concentrations (>5%). Ethylene might therefore act as a surface hydrogen and C_1 intermediates scavenger [20], thus reducing methane formation. Ethylene addition also enhanced C_{3+} hydrocarbon formation. However, the few studies that investigated the effect of ethylene on long chain hydrocarbons have shown that the influence of ethylene on the rate of hydrocarbon production decreases with increasing carbon number [9,11,19,25]. Thus, the chain growth probability of high carbon number species ($>C_{10}$–C_{12}), is not affected by ethylene initiation. On the other hand, Patzlaff et al. [11] have shown that secondary chain growth of readsorbed α-olefins is characterised by a lower growth probability and is relatively low for cobalt catalyst (and negligible for iron catalysts).

To gain more insight into the role of olefin secondary hydrogenation on the FTS mechanism, other co-feeding studies with light 1-alkenes (C_3–C_6) have been performed as model reactions. They have shown similar effects on the FTS mechanism to those using C_2 probes, i.e. that added 1-alkenes act mainly as chain initiators [1,9,19,27–32], and increase the formation rates of compounds with higher carbon numbers than the added alkenes. However, this increase in formation rate is only observed for hydrocarbons with a carbon number below C_{12}–C_{15}. In standard FTS, olefins produced are more likely and to a larger extent, to re-adsorb on the catalyst surface and to participate in further chain growth, rather than being hydrogenated to paraffins. However, it is expected that olefin re-adsorption might not affect the distribution and chain growth probability of higher carbon number species. Shi and Davis [19] suggested that olefins might also serve as chain termination species, or that they can function as a monomers for insertion into the growing chain, being incorporated only once. The extent of conversion of the added olefins also revealed a strong carbon number dependence, mainly due to carbon number dependent solubility of the olefins in the liquid reaction product [9].

In addition to 1-alkenes, acetylenic compounds [33,34], and in particular acetylene [27,35,36], have also been used as probe molecules. Acetylene competes very effectively with CO for adsorption on active sites and is adsorbed more strongly on catalyst surfaces than CO [33]. It will initiate chain growth at C_2, thus by-passing methane formation [33] and increasing C_{3+} selectivity. However, as C_2 species are not easily able to add to growing chains, acetylene does not act as a chain propagator and is incorporated into the product only once [36].

The mechanisms for ethylene and acetylene adsorption on the catalyst surface appear to be very similar. However, acetylene incorporation is much greater than any other acetylenic molecules, and acetylene is generally more strongly adsorbed on FT catalysts than light 1-alkenes, thus making it a more efficient chain initiator at lower temperatures. It is suspected that acetylene is first adsorbed on the catalyst surface and hydrogenated to form ethylidyne (Fig. 2) [36], which then remodels the catalyst surface, allowing CO from the syngas to bind briefly, and react with H_2 to form growing chains.

According to some authors, α-olefin secondary hydrogenation and chain growth by the CH_2 insertion mechanism alone does not satisfactorily explain the observed deviations from the ASF distribution, as shown by the co-feeding experiments discussed above. Indeed, as mentioned previously, when ^{14}C-ethylene was added to the syngas feed, only 30% of it was used for secondary chain growth [9,11,19,25]. In addition, the rate of olefin insertion decreases with increasing chain length of the propagating hydrocarbons, with added olefins not incorporated into higher hydrocarbons

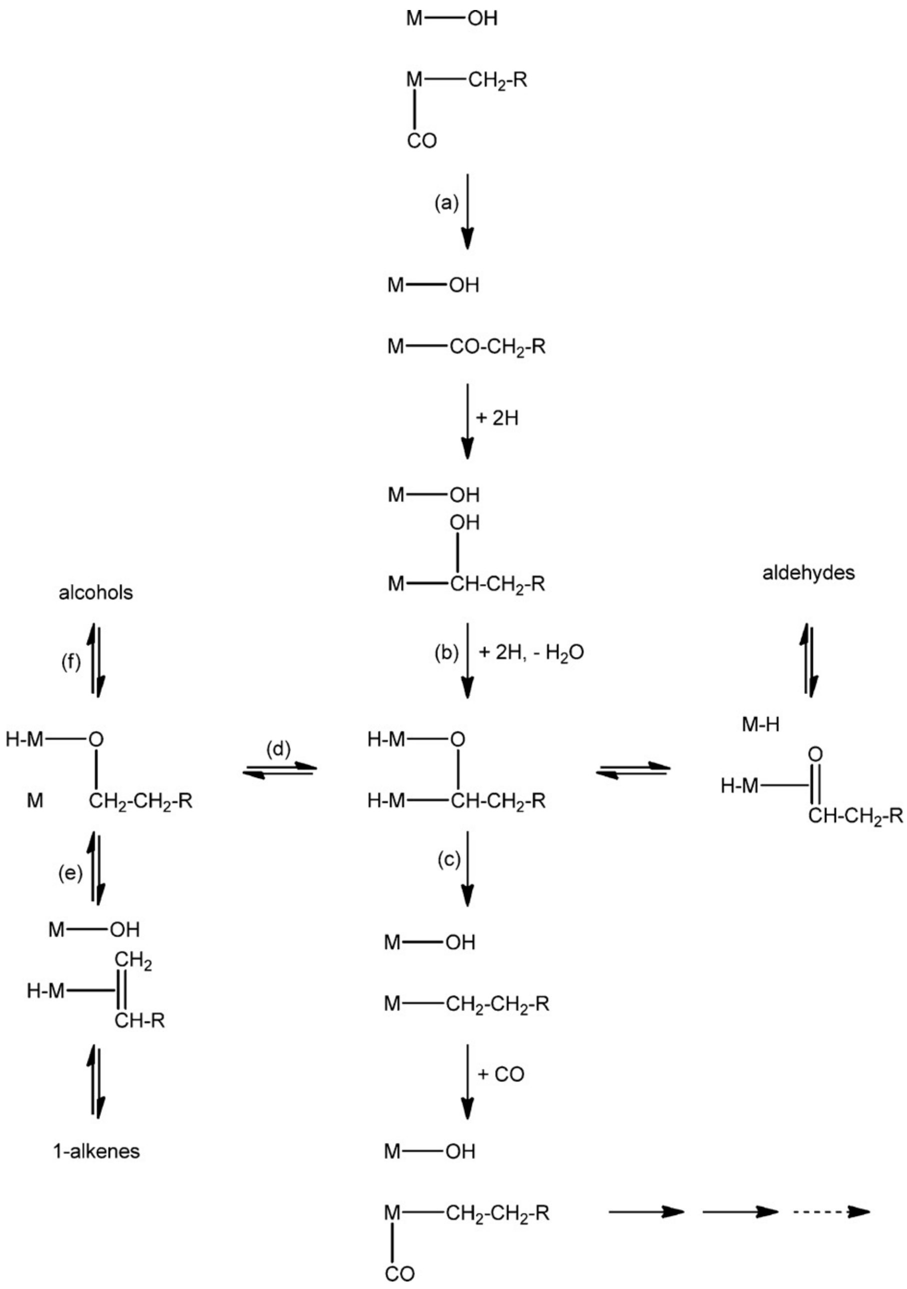

Fig. 3. CO insertion mechanism [1].

(generally above C_{15+}). As a consequence, if α_1 characterised the product distribution of species affected by olefin re-adsorption, longer chain hydrocarbons, not affected by olefin re-adsorption, could be characterised by a different, higher chain growth probability, α_2, resulting from a different, superimposed chain growth mechanism [25].

3. Oxygenate formation

The formation of the full range of products (hydrocarbons, oxygenates, CO_2, etc.) during the FTS cannot be the result of the CH_2 insertion mechanism alone. While hydrocarbons are mostly formed through this mechanism, it does not fully explain the presence of oxygenates in the reaction products. Dry proposed a different, parallel mechanism to the CH_2 insertion mechanism: the CO insertion mechanism, where CO acts as the monomer [38]. Alcohol addition to the FTS was used to investigate this mechanism further.

Addition of ethanol (up to 6%) during the FTS over a Co catalyst was found to increase the selectivity of light products and increase the olefin to paraffin ratio, while at the same time decreasing the catalyst's activity [39]. Methanol co-feeding had the same effect on the catalyst, but also increased methane, water, and CO_2 selectivity [40]. Isotopic tracer studies show that alcohols initiate chain growth but do not propagate chain growth during the FTS [41]. Shi and Davis [19] have shown that co-fed ethanol initiated chain growth 50–100 times more effectively than ethylene, thus increasing the rate of hydrocarbon formation.

Tau et al. postulated that, when alcohol is added to the reaction mixture, an alcohol intermediate might act to produce Fischer–Tropsch products in a reaction pathway different, and in parallel to the methylene insertion mechanism [41]. This was confirmed by Gaube and Klein, who assumed that the added alcohols are incorporated and participate in the chain growth via the CO insertion mechanism, which is characterised by the higher growth probability of the resulting ASF distribution [1]. Oxygenates might also re-adsorb over the catalyst surface and take part in corresponding secondary reactions [42] (chain growth and hydrogenation to the corresponding hydrocarbons), effectively competing with olefin secondary hydrogenation, which would explain the observed increase in the olefin to paraffin ratio. They also undergo direct hydrogenolysis to eliminate water and to produce the corresponding alkane.

Gaube and Klein [1] proposed a mechanism to clarify oxygenate formation based on the hypothesis that two competitive and incompatible chain growth mechanisms are involved: methylene insertion, as described above, and CO insertion. Each of these two mechanisms presents a different ASF distribution with different chain growth probabilities.

The CO monomer insertion mechanism (Fig. 3) is initiated by insertion of CO by alkyl migration (a), reductive elimination of water (b), followed by C–O cleavage (c) by altogether four H equivalents leading back to the starting situation. Termination can occur by conversion of the C,O-bridging aldehyde intermediate to alcoholate (d), which is either dehydrated via β-C–H activation (e) to afford an M–OH function and a hydrido (olefin) metal species, or, to a minor extent, is converted to alcohols (f). As the termination route is reversible, co-fed alcohols can cause initiation via the C,O-bridging aldehyde intermediate.

The observed decline in catalyst activity may be the result of the instantaneous oxidation of the metallic cobalt by alcohols and the formation of cobalt-support species, such as silicate or hydrosilicate species when silica is used as support. As for water, these effects are reversible and normal FT activities are observed when alcohols are removed from the feed. Jalama et al. [39] have suggested that the reversible effect was due to the possible re-reduction of oxidised CoO species to Co metal by the hydrogen contained in the syngas.

4. Fischer–Tropsch by-product formation

4.1. Water

Water is a primary, albeit undesirable, product of the FTS (Eq. (1)). CO conversion, the reactor system, and the nature of the catalysts used will influence the amount of water formed, which generally increases with time-on-stream and along the reactor. The effect of water on the FTS is quite complex and mostly depends on the catalyst's characteristics, i.e. support (type and pore size), metal nature and loading (dispersion and cluster size), additives (e.g. noble metals and other dopants), and preparation procedure. Dalai and Davis [43] have performed a comprehensive literature review on the effect of water on the performance of both supported and unsupported cobalt catalysts, highlights of which are briefly described here.

For unsupported cobalt oxide catalysts, water added to the reaction (up to 30 vol.%) had some positive effects on CO conversion, C_{5+} selectivity, and olefin selectivity while at the same time reducing methane and CO_2 selectivity. The increase in CO reactivity in the presence of water might be due to the direct interaction between co-adsorbed CO and water that lowers the barrier to CO dissociation, while an increase in surface concentration of active carbon at increased water partial pressure could explain the positive effect on selectivity. However, above a certain concentration of added water (∼30 vol.%), CO conversion no longer increases and the catalysts are permanently damaged.

For supported cobalt catalysts the effect of water is different depending on the support and the amount of added water [44]: while water has a positive effect on CO conversion on silica-supported catalysts and to a lesser extent, on titania-supported catalysts, alumina supported catalysts deactivate when water is added. However, above a certain water partial pressure ($p_{H2O}/p_{H2} > 0.6$), the effects of water on CO conversion are generally negative and irreversible for all catalysts. Regarding selectivity, both indigenous and water added to syngas led to a marked increase in C_{5+} selectivity and a decrease in CH_4 selectivity for all of the Co catalyst systems, again below a certain water concentration, depending on the catalyst.

Dalai and Davis [43] proposed three possible scenarios or combinations of these to explain the results observed for the addition of water to cobalt catalysts as reported in the literature:

1. The negative effect of water can be the result of catalyst re-oxidation, which can occur at high water partial pressure and is dependent on the ratio of hydrogen and water partial pressures in the reactor and the Co crystallite size. Alternative catalytic cobalt species can then form, some of which might be inactive.
2. The effect of water is influenced by the support average pore diameter. For wide pore diameter supports, where the active sites are mostly present within the pores of the support, water can adsorb and form water-rich intra-pellet liquids, which alter the pore filling behaviour by heavier hydrocarbons, and reduce transport restrictions. It can therefore be assumed that for smaller pores, water can restrict access to the active catalyst sites, thus reducing the activity of the catalyst. This can also explain the deactivation effect of water at higher concentrations.
3. Water can have a reversible kinetic effect and lower the barriers to CO dissociation and inhibit the secondary hydrogenation of olefin products as a result of the competitive adsorption of water.

4.2. CO_2

CO_2, like water, is a by-product of the FTS, and its production represents a reduction in carbon utilisation efficiency. As for water formation, which results from the reaction of adsorbed oxygen on the catalyst surface formed during the CO dissociation step with adsorbed hydrogen, CO_2 can be formed from the reaction between adsorbed oxygen and adsorbed CO. It can also result from the water gas shift (WGS) reaction (Eq. (3)). Formation of CO_2 on iron-based catalysts is generally more important compared to cobalt-based catalysts, due to the much higher WGS activity of Fe catalysts.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

The influence of CO_2 on the catalytic performance of Fe-based catalysts [45–47] and Co-based catalysts [48] for the FTS has been studied, using selective CO_2 addition to the syngas.

CO_2 addition to the FTS on Fe-based catalysts does not particularly affect the catalyst activity or the CO_2 formation rate. However, it increases the rate of the reverse WGS reaction [46,47]. Liu et al. and Krishnamoorthy et al. both concluded that addition of CO_2 to the syngas feed would therefore increase the water concentration and, consequently, the oxygenate formation rate. In turn, this leads to a decrease in the net concentration of surface H_2, to a lower average H_2/CO ratio throughout the catalyst bed, and therefore to a higher olefin to paraffin ratio. In addition, while CO_2 can act as a chain initiator to produce both oxygenates and hydrocarbons, it does not contribute to a measurable extent to chain growth, which is mostly promoted through intermediates from CO [49,50]. Zhang et al. have suggested conversion of CO and CO_2 occurs by different reaction pathways, from the hydrogenation and breaking of two C–O bonds in CO_2 [51]. In addition, studies using addition of isotopic CO_2 have shown no particular enrichment of the hydrocarbon products, indicating that CO_2 is much less reactive than CO in chain initiation and growth [47,49].

Cobalt-based catalysts have a lower activity towards the WGS reaction. Thus, CO_2 appears to have little influence on Co-based catalysts. Indeed, Riedel and Schaub have shown that no measurable hydrocarbon production from CO_2 could be found under typical Fischer–Tropsch conditions, with CO_2 behaving as an inert gas component [52], which can be explained by the very slow hydrogenation rate of CO_2 in the presence of CO [51].

5. Conclusion

It has been shown that additives such as small 1-alkenes, alcohols, or CO_2, act as chain initiators for the FTS, and both probe-initiated and conventional FTS proceed simultaneously, with their respective products overlapping. The majority of work in this area has shown that probe molecules do not contribute to chain growth, although added olefins and alcohols have been shown to be incorporated into FTS products, usually through chain initiation.

However, to date, the effects and influences of the additives discussed in this paper on the overall product distributions and on the catalysts activity have not been thoroughly investigated. As co-feeding experiments have shown, olefins adsorb on the catalyst surface and influence the overall FTS product distribution. It could therefore be envisaged that additives such as olefins could be used in the FTS to modify the catalyst surface, e.g. by selectively binding to and/or inhibiting certain active sites such as those promoting chain growth of higher hydrocarbons, or secondary hydrogenation, in order to improve the overall efficiency and selectivity of the process.

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