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Organometallic chemistry and surface science: mechanistic models for the Fischer–Tropsch synthesis

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Abstract

The Fischer–Tropsch synthesis is an industrially important process for the conversion of synthesis gas (CO/H_2) into hydrocarbons and oxygenates. Synthesis gas can be obtained from coal or natural gas. Organometallic model complexes and surface science techniques have been widely used to obtain mechanistic information about this heterogeneous process. A review of the mechanisms for the Fischer–Tropsch synthesis and the evidence for these mechanisms is presented. It is generally accepted that the Fischer–Tropsch reaction may be viewed as a polymerisation of surface methylene ($=CH_2$) species, which are formed by the dissociation and hydrogenation of CO on the catalyst surface. The alkyl mechanism proposes that the reaction is initiated by the formation of a surface methyl species, and that chain growth takes place by successive insertions of methylene into the metal-alkyl bond. The alkenyl mechanism proposes that the formation of a surface vinyl species ($–CH=CH_2$) initiates chain formation, and that chain growth is facilitated by methylene insertion into the metal-vinyl bond to form an allyl species ($–CH_2–CH=CH_2$). The allyl species isomerises to form a surface alkenyl ($–CH=CH–CH_3$) which may propagate further. These mechanisms are discussed.

Keywords: Fischer–Tropsch; Organometallic chemistry; Mechanisms; Alkyl; Alkenyl

1. Introduction

1.1. Historical and economic significance of the Fischer–Tropsch synthesis

The hydrogenation of carbon monoxide over a late transition metal catalyst to form predominantly linear hydrocarbons and/or oxygenates has come to be called the Fischer–Tropsch synthesis [1]. Early observations of catalytic carbon monoxide hydrogenation reactions were made by Sabatier and Senderens in 1902 (methanation over a nickel catalyst) [2] and BASF in 1913 (high pressure synthesis of hydrocarbons and oxygenates over a cobalt catalyst) [3]. The major breakthrough in the field came in the 1920s when Frans Fischer and Hans Tropsch announced the synthesis of hydrocarbons at atmospheric pressure over iron and cobalt catalysts [4].

The history of the Fischer–Tropsch process has been influenced by the political and economic fortunes of nations, as up till now it has only been economic for countries with abundant coal and limited access to oil. Germany commercialised the process in the 1930s in order to achieve self sufficiency in liquid fuels, and during World War II it relied heavily on Fischer–Tropsch technology to fuel its armies [5].

After World War II the vast oil reserves of the Middle East began to be fully exploited and the Fischer–Tropsch process became uneconomic in Germany. Interest in the process remained however, particularly in the United States of America and South Africa. South Africa has no oil of its own but has extensive coal deposits which could be utilised to produce liquid fuels. A government-backed company, South African Synthetic Oil Limited (SASOL), was formed in South Africa in 1950 to produce liquid fuels from coal. Fischer–Tropsch technology became increasingly important to South Africa during the 1970s as a result of high world oil prices and international sanctions that included an oil embargo. The decline in world oil prices from the mid 1980s led SASOL to move in the direction of increased chemicals production from the Fischer–Tropsch process as these could be sold for much higher prices. Expansion into Fischer–Tropsch based chemicals production is today a major aim of SASOL [6].

There are currently a number of companies pursuing Fischer–Tropsch technology either through research, pilot plants, or planned large-scale plants. The companies include the Royal Dutch/Shell group, which built a plant based on natural gas in Sarawak in 1992, Exxon, Syntroleum, Rentech, Texaco, ARCO and Enron. SASOL and Chevron have recently announced large-scale Fischer–Tropsch joint ventures based on natural gas reserves in Nigeria and the Middle East.

1.2. Synthesis gas formation

Synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is the feedstock for all Fischer–Tropsch processes. Syngas is obtained by gasifying coal or reforming natural gas (methane) with steam. Historically coal gasification has primarily been used for the production of syngas due to the low cost and transportability of coal. However, coal gasification is an inefficient process, with approximately 50% carbon loss due to the formation of CO_2 [7]. The reformation of methane is more efficient, with approximately 70% carbon conversion to CO [7], and it is likely that Fischer–Tropsch projects of the future will use methane as the source of syngas. Thus, the recently announced joint venture between SASOL and Chevron will exploit natural gas reserves in Nigeria and the Middle East.

2. Fischer–Tropsch mechanisms and the relevance of organometallic chemistry and surface science

In the light of the potential economic importance of Fischer–Tropsch chemistry, a detailed mechanistic understanding of the process is highly desirable. Such an understanding might enable the industrial applications of the reaction to be made more efficient. At the present time, however, the mechanism of the Fischer–Tropsch reaction is still not fully understood. The Fischer–Tropsch reaction yields predominantly straight chain hydrocarbons (α-olefins and alkanes) and there is general agreement that the reaction may be viewed as a methylene polymerisation reaction where the monomer unit ($=CH_2$), is not initially present. The products are formed by hydrogenation of CO to generate the methylene monomer, initiation of chain growth and competing chain propagation and chain termination steps. Analyses of the product distributions show that they obey Anderson–Schultz–Flory chain-length statistics (Eq. (1)):

$$\log\left(\frac{w_i}{i}\right) = i \log \alpha + \log\left(\frac{(1-\alpha)^2}{\alpha}\right) \tag{1}$$

where w_i is the weight fraction of product, i is the length of the hydrocarbon chain, and α is the probability of chain growth, the value of which is dependant on temperature, catalyst, CO/H_2 ratio and pressure.

This distribution implies that sequential chain propagation steps result in the formation of the hydrocarbon chain one carbon unit at a time, and that chain propagation and termination occur with probabilities that are approximately independent of chain length. The mechanism for the Fischer–Tropsch reaction must therefore be consistent with the Anderson–Schultz–Flory distribution, although modifications may be necessary to take account of the nature of the catalyst particles [8,9]. The task of elucidating the mechanism is made more difficult by a number of factors:

- The reaction produces a large number of different products, making the study of the formation of a single compound more difficult. Both primary products (i.e. products formed on the catalyst by the hydrogenation of CO) and secondary products (i.e. products resulting from the reabsorption and modification of primary products) are present in Fischer–Tropsch product distributions.
- Direct observation of the species reacting on the catalyst surface is often not possible. Most observation techniques require low temperature and/or pressure conditions which are far removed from actual reaction conditions. Those surface species that are observed are usually long-lived species which are by definition not very reactive, and therefore unlikely to be involved as intermediates in the catalytic reaction.
- A wide variety of catalysts are active for the reaction, including iron, cobalt, ruthenium and rhodium. It is not always clear whether a proposed mechanism on one type of catalyst is necessarily applicable to other catalysts. This is made more complex by the effects of catalyst supports and promoter effects.

One way of overcoming the difficulties of observing intermediates directly on the catalyst surface is to synthesise and study well-defined organometallic species which resemble the proposed intermediates. The properties and reactivity of these model compounds may be tuned by altering ligands and reaction conditions, thus allowing the researcher to mimic the properties of a heterogeneous catalyst surface in a controlled manner. The validity of the relationship between organometallic chemistry and chemistry occurring on metal surfaces is now widely recognised [10–13]. Organometallic models have been extensively employed and many of the results are referred to in the following discussion. The techniques of surface science have also been successfully used to elucidate some mechanistic information about Fischer–Tropsch reactions. Well-defined single crystal surfaces under ultrahigh vacuum conditions are used as model surfaces for heterogeneous catalysts. Observations of reactions occurring on the surface can be made using techniques of surface science such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD) and mass spectrometry [14]. While the value of surface science model experiments is limited by vast differences in temperature and pressure from Fischer–Tropsch conditions, key steps in a proposed mechanism can usefully be studied under highly controlled conditions, where only a small number of surface species are present.

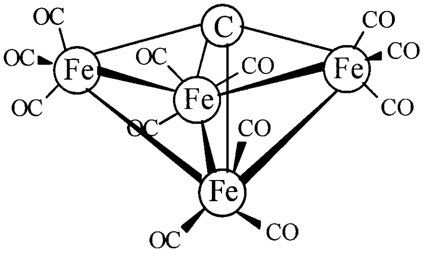
3. Formation of methylene species: generation of the 'monomer'

The majority of the products of the Fischer–Tropsch synthesis are linear hydrocarbons, and it is the mode of their formation that is the focus of most mechanistic studies. It is widely accepted that the reaction may be viewed as a polymerisation of methylene units, as originally proposed by Fischer and Tropsch themselves [15]. Several other mechanisms have been proposed at various times, including mechanisms involving hydroxymethylene species [16] and carbonyl insertion [17]. The CO insertion mechanism for chain growth (successive CO insertions and hydrogenations of the resulting acyl species) has lost favour due to the observation that most catalysts active for the Fischer–Tropsch reaction also dissociate CO when it is absorbed on the surface at Fischer–Tropsch reaction temperatures [18]. However a CO insertion step is often invoked to account for the formation of oxygenates, usually with terminal functionality (see Section 4.7).

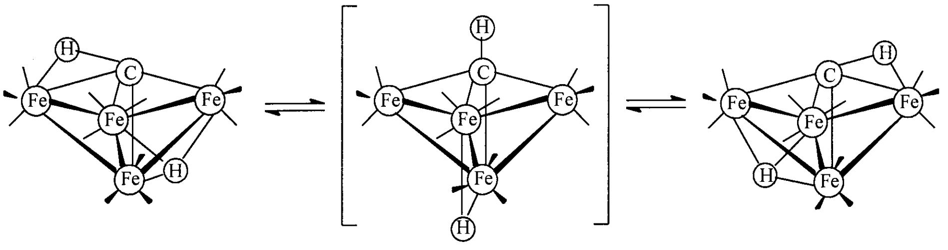
It is widely accepted that initiation of the Fischer–Tropsch process involves the absorption and subsequent dissociation of CO on the surface. This is supported by both experimental evidence and theoretical study [19]. It is unclear whether H_2 dissociates on the catalyst surface as well; most sources however accept the dissociation of H_2 to form surface hydride species. Reaction of hydrogen with surface carbon (carbide) atoms leads sequentially to the formation of surface methyne ($\equiv$CH) and methylene ($=CH_2$). The methylene units thus formed are the monomer units of the overall polymerisation reaction.

Studies on organometallic compounds have confirmed that species such as C and CH can act as ligands [20–22]. The compound $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ (Fig. 1) is an example of a cluster containing exposed carbide in an arrangement that could be analogous to carbide on a metal surface. Similarly, the compound $[HFe_4(CH)(CO)_{12}]$ (Fig. 1) contains a methyne (CH) ligand bound through both the C and the H atoms to the array of iron atoms [23].

There is ample evidence for the existence of surface methylene species. Brady and Pettit found that passing a mixture of diazomethane (CH_2N_2) and an inert gas such as helium over Ni, Pd, Fe, Co, Ru or Cu surfaces resulted in the decomposition of the diazomethane to form nitrogen and ethylene [24]. This result is explained by the formation and subsequent coupling of methylene species on the metal surface (Fig. 2). When H_2 was added to the mixture, a range of hydrocarbon products was formed (see below).



a) Structure of $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$



b) Structure of $HFe_4(\mu_4\text{-}CH)(CO)_{12}$ (CO ligands not shown)

Fig. 1. Model compounds for surface C and CH.

Akita and co-workers have demonstrated the reduction of bridging carbonyl ligands to form bridging methylene ligands in a diruthenium complex (Eq. (2)) [25]. Using H_2SiEt_2 as an H_2 equivalent, reduction of $[Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$) at 150°C in toluene resulted in the formation of a mixture of $[Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(CO)_2]$ and $[Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2]$. ^{13}C and deuterium labelling studies confirmed that the products arose from reduction of the μ-CO ligands. This reaction is a model for the hydrogenation of CO on the Fischer–Tropsch catalyst surface to form surface methylene species.

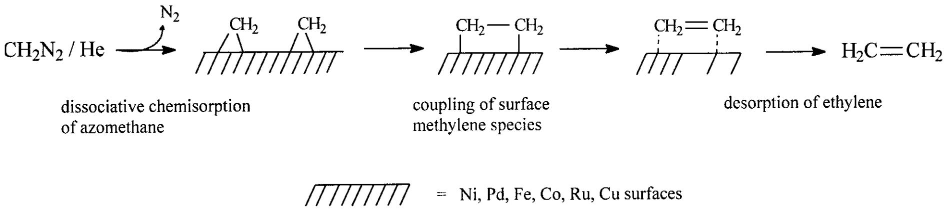
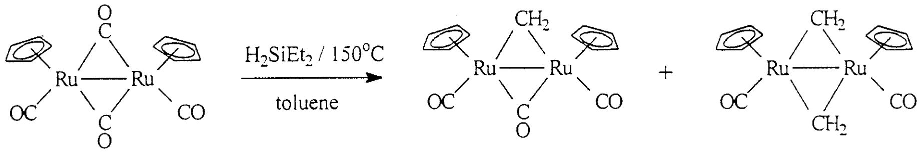


Fig. 2. Ethylene formation by coupling of surface methylene species.



(2)

Numerous other methylene-containing model complexes of Fischer–Tropsch active metals including Rh [26], Ru [27,28], Co [29] and Fe [30] have been made and characterised.

4. Alkyl mechanism for chain propagation and termination

The alkyl mechanism for the Fischer–Tropsch reaction was first proposed by Brady and Pettit [24,31]. They observed that when diazomethane was passed over catalysts such as Ni, Pd, Fe, Co, Ru or Cu, the primary product was ethylene, resulting from the coupling of two surface methylene species (see above). However, when H_2 was mixed with diazomethane and passed over the catalyst, a range of hydrocarbons similar to the product distribution of the Fischer–Tropsch reaction was formed. They concluded that there is a reaction between surface methylene and surface hydrogen to form a surface methyl, and that chain growth is propagated by successive insertions of methylene into the metal-alkyl bond (Fig. 3). Termination of the chain growth takes place by means of a β-hydride elimination to give α-olefins or a reduction by surface hydride to give alkanes.

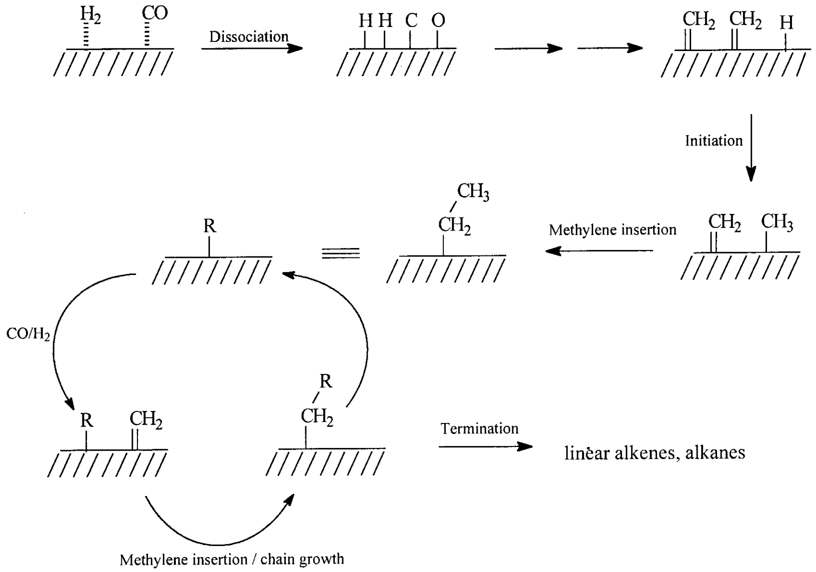


Fig. 3. The alkyl mechanism for initiation and chain growth in the Fischer–Tropsch reaction.

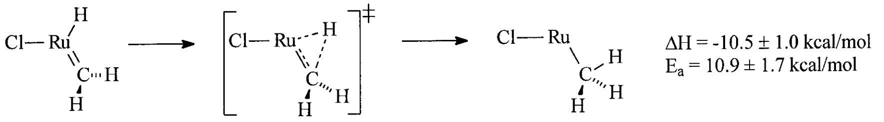


Fig. 4. Computational model for the insertion of methylene into a ruthenium–hydrogen bond.

4.1. Evidence for the formation of a surface methyl species

The interaction between methylene and surface hydrogen to form a surface methyl group has been modelled by ab initio methods for the hypothetical ruthenium model complex [RuClH(=CH_2)] [32]. The calculations of Goddard and Carter indicate that the insertion of methylene into the Ru–H bond (Fig. 4) is facile, exothermic, and proceeds with a low energy barrier (~ 10.9 kcal/mol). In addition Bercaw and co-workers have observed methylene insertion directly in the compound [$Cp^*_2Ta(H)(=CH_2)$] ($Cp^* = \eta^5$-C_5Me_5) by means of magnetisation transfer experiments (Fig. 5) [33]. The 16 electron species [$Cp^*_2TaCH_3$] was then trapped under an atmosphere of CO to give the product [$Cp^*_2Ta(CH_3)(CO)$] (Fig. 5). The formation of a surface methyl group completes the initiation step of the mechanism.

4.2. Evidence for methylene insertion into a surface alkyl species

The propagation, or chain growth, step of the mechanism involves the insertion of surface methylene species into the metal-methyl bond of the surface methyl group to form a surface ethyl group. Calculations by Goddard and Carter on hypothetical [$RuCl(CH_3)(=CH_2)$] indicate that methylene insertion into the metal-methyl bond is also exothermic and kinetically feasible [32]. Given the predominance of long chain hydrocarbons formed over ruthenium heterogeneous catalysts, the chain propagation step (insertion into a metal–alkyl bond) must in fact be more favourable than the initiation step (insertion into a metal–hydrogen bond) on ruthenium metal surfaces.

Several studies on model compounds have experimentally demonstrated methylene insertion into alkyl species. Werner and co-workers have, for example, found that treatment of [$(C_6Me_6)Ru(CH_3)_2(PPh_3)$] with [$CPh_3$]$PF_6$ (trityl hexafluorophosphate) resulted in the formation of the ethylene(hydrido) complex [$(C_6Me_6)RuH(C_2H_4)(PPh_3)$] [34]. They postulated that the trityl cation must abstract a hydride from a methyl to form a transient ruthenium–methylidene–methyl complex, which

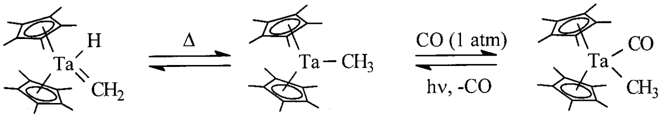


Fig. 5. Methylene insertion into Ta–H bond and CO trapping of the resulting 16-electron methyl complex.

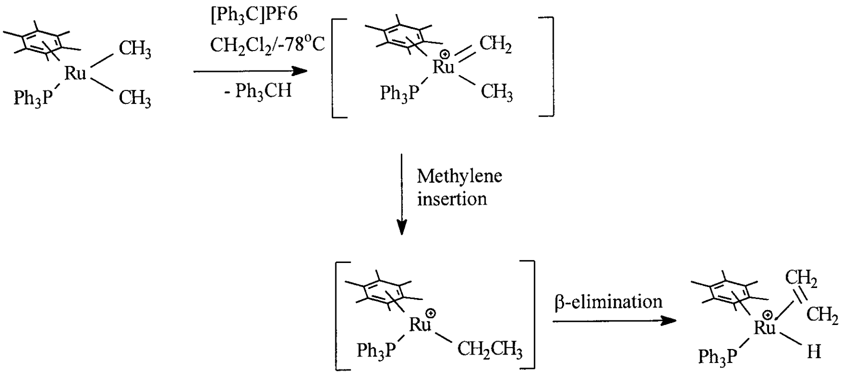


Fig. 6. Methylene insertion into a ruthenium–methyl bond, followed by β-elimination.

then undergoes methylene insertion into the ruthenium–methyl bond and β-hydride elimination to yield the ethylene(hydrido) product (Fig. 6). Cooper and Hayes did similar experiments to demonstrate methylene insertion on a paramagnetic cationic tungsten complex. Thus, treatment of $[Cp_2W(CH_3)_2]PF_6$ with a source of trityl radicals ($CPh_3^{\bullet}$) resulted in the formation of $[Cp_2W(C_2H_4)H]PF_6$ [35]. The proposed mechanism involved the formation of a methylidene–methyl intermediate by abstraction of a hydrogen radical, methylene insertion into the tungsten-methyl bond and β-hydride elimination to yield the observed product. When the reaction was carried out in the presence of PMe_2Ph, $[Cp_2W(CH_3)(CH_2PMe_2Ph)]PF_6$ and $[Cp_2W(CH_2CH_3)(PMe_2Ph)]PF_6$ were trapped, thus providing evidence for the intermediacy of the proposed methylidene–methyl- and ethyl intermediates respectively (c.f. Fig. 6).

In the Fischer–Tropsch reaction, the surface ethyl can then react in turn with further methylene units sequentially, thus effecting chain growth. Methylene insertion into a metal–ethyl bond has been demonstrated by Cooper and Hayes with the complex $[Cp_2W(CH_3)(C_2H_5)]$ [36]. In the presence of $[CPh_3]BF_4$, the product $[Cp_2W(C_3H_6)H]BF_4$ was formed. Two possible routes were proposed; involving methylidene-ethyl and ethylidene-methyl intermediates, respectively (Fig. 7). However, when the labelled complex $[Cp_2W(CD_3)(C_2H_5)]PF_6$ was treated with $[CPh_3]BF_4$ in the presence of PMe_2Ph, the product $[Cp_2W(CD_2PMe_2Ph)(C_2H_5)]PF_6$ was exclusively isolated. This ‘trapping’ experiment indicates that the methylidene–ethyl complex $[Cp_2W(CH_2)(C_2H_5)]PF_6$ is the key intermediate. The reaction then proceeds via methylene insertion into the metal–ethyl bond and subsequent β-hydrogen elimination to yield the (propene)hydrido product (Fig. 7).

Experiments have also been devised to isolate the proposed surface alkyl intermediates present in heterogeneous Fischer–Tropsch syntheses. Thus, Ekerdt and Wang have developed a scavenging technique using pyridine to identify surface intermediates [37]. They found that pyridine reacts with surface alkyl species to form α-alkyl pyridine products. In a Fischer–Tropsch synthesis over a heterogeneous iron catalyst, they detected as major scavenged components 2-methylpyridine, 2-ethylpyridine and 2-propylpyridine. This provides further support for the existence of surface alkyl intermediates in the Fischer–Tropsch reaction.

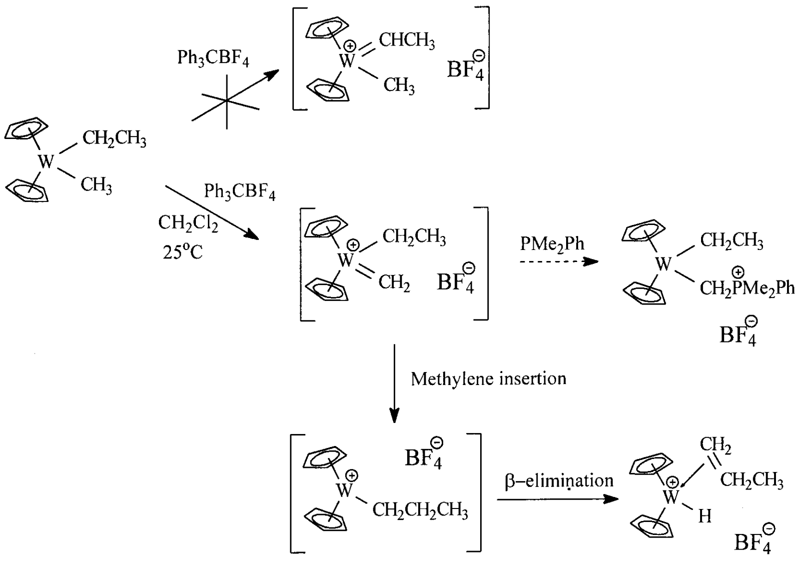


Fig. 7. Methylene insertion into a tungsten–ethyl bond. Trapping experiments with PMe_2Ph and deuterium labelling experiments indicate that the mechanism proceeds via a methylidene–ethyl intermediate.

Alkyl complexes containing Fischer–Tropsch active metals have been known for some time. Complexes with alkyl groups extending to more than six carbon atoms in the chain have been synthesised and characterised and aspects of their reactivity have been studied [38–40].

4.3. Simulation of the Fischer–Tropsch reaction on a single crystal surface

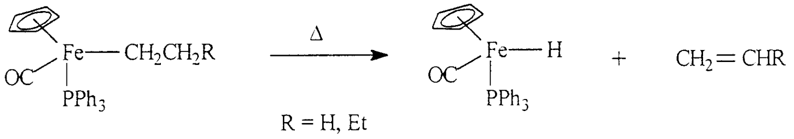
The most recent evidence presented in support of the alkyl mechanism has been put forward by Stair and Kim based on an investigation of the surface chemistry of adsorbed methyl radicals on oxygen-modified Mo(100) surfaces under ultrahigh vacuum (UHV) conditions [41]. While many investigations of the chemistry of alkyl fragments on single crystal surfaces have been made, the unique features of the oxygen-modified Mo(100) surface and the novel method of generating the surface methyl species have resulted in a temperature programmed desorption (TPD) product distribution resembling that of the Fischer–Tropsch synthesis more accurately than any previous study. Thus a Mo(100) surface with a 0.9 monolayer coverage of oxygen was dosed to saturation with methyl radicals generated by pyrolysis of azomethane ($CH_3N_2CH_3$) in a quartz tube. TPD was carried out over a 300–1000 K temperature range, and the volatile products were detected by mass spectrometry. The major product was methane, formed by the hydrogenation of surface methyl fragments by surface hydrogen. The presence of surface hydrogen implies that a proportion of the methyl fragments have dehydrogenated to form surface methylene (or methyne) species. The other products observed are C_2 to C_5

α-olefins. The yields of these olefins approximately obey the Anderson–Schultz–Flory distribution characteristic of the Fischer–Tropsch synthesis: the log(yield) decreases linearly with increasing chain length. The authors therefore propose that the chain growth arises as a result of sequential methylene insertions into surface metal-alkyl bonds, which occur in this case with a probability of ~0.3, and that β-hydride elimination (probability 0.7) and subsequent desorption result in the observed distribution of olefinic products. Alkanes other than methane are not observed, because the surface hydrogen is primarily consumed by the hydrogenation of methyl fragments.

4.4. β-hydride elimination: formation of linear α-olefins

Termination of the chain growth can occur via several routes. α-Olefins (1-alkenes) may be formed through a β-hydride elimination reaction, forming a terminal double bond [24,42,43] (Fig. 8). After β-hydride elimination the weakly co-ordinated alkene desorbs from the surface yielding the product.

Numerous studies have established the β-hydride elimination reaction as a fundamental reaction in organometallic chemistry [44]. Reger and Culbertson observed that the primary decomposition products of [CpFe(CO)(PPh$_3$)(alkyl)] were olefins and the metal hydride [CpFe(H)(CO)(PPh$_3$)] (Eq. (3)) [45]. They inferred that a β-hydride elimination step must be involved.



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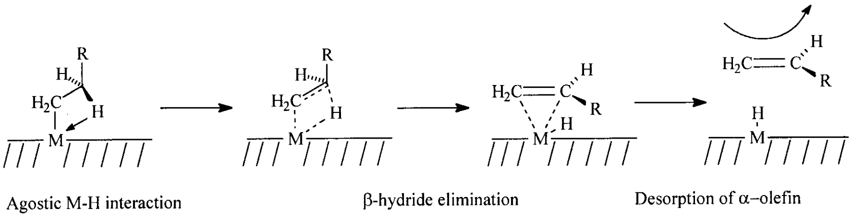
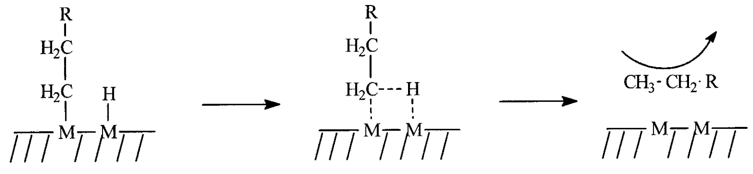


a) β-elimination mechanism for the formation of α-olefins



b) Surface hydride reduction of alkyl chain for the formation of alkanes

Fig. 8. Proposed chain termination mechanisms in the Fischer–Tropsch reaction.

In addition several studies on the decomposition of alkyl species on single crystal metal surfaces have been reported [46–48]. Surface alkyl species were generated by the thermal dissociation of alkyl iodides, and were observed by means of high-resolution electron energy loss spectroscopy (HREELS). During thermal programmed desorption experiments, the primary decomposition products were linear α-olefins. Deuterium labelled 1-iodopropane-2,2-d_2 decomposed to form propylene-d_1, thus indicating that β-hydride elimination is the mechanistic pathway for decomposition [47].

Ethylene can also be formed through the coupling of two surface methylene species, followed by desorption from the surface. This reaction was demonstrated by Brady and Pettit in their experiments with diazomethane on metal surfaces [24].

4.5. Reduction by surface hydride: formation of linear alkanes

An alternative termination reaction, which results in the formation of linear alkanes, occurs when surface hydrogen reduces the surface alkyl species (Fig. 8). It has been observed in several decomposition studies of metal–alkyl compounds that a significant amount of alkane is formed along with the corresponding olefin. Whitesides and co-workers found that *n*-butyl-copper(I) compounds decompose to form 1-butene and *n*-butane [49]. Deuterium labelling studies, using an *n*-butyl-2,2-d_2-copper(I) compound, indicate that 1-butene-d_1 is formed by a β-hydride elimination pathway (Eq. (4)). The butane is found to be butane-d_3, which implies that it is formed by the reduction of the *n*-butyl-2,2-d_2-copper(I) compound by the copper deuteride product of β-hydride elimination (Eq. (5)). This reductive step occurred at a rate competitive with β-hydride elimination, and the resulting product mixture contained an approximately 1:1 ratio of 1-butene to *n*-butane.

$$(PR_3)CuCH_2CD_2CH_2CH_3 \xrightarrow{\beta\text{-elimination}} CH_2{=}CDCH_2CH_3 + (PR_3)CuD \quad (4)$$

$$(PR_3)CuCH_2CD_2CH_2CH_3 + (PR_3)CuD \xrightarrow{\text{reduction}} CH_2DCD_2CH_2CH_3 + Cu + PR_3$$
$$[PR_3{=}P(n\text{-}Bu)_3] \quad (5)$$

Wegner and Sterling compared mononuclear and binuclear iron alkyl complexes which decompose to form a mixture of olefins and alkanes as organic decomposition products [50]. Decomposition of a complex with two metal-alkyl groups ($[Me_2Si(\eta^5\text{-}C_5H_4Fe(CO)_2C_5H_{11})_2]$) was shown to produce a higher proportion of alkane than that of a complex with a single metal-alkyl group ($[\eta^5\text{-}C_5H_5Fe(CO)_2C_5H_{11}]$) (Fig. 9). This suggests that the source of the hydrogen in the alkyl reduction is the metal-hydride product of β-hydride elimination, which is in closer proximity during the decomposition of the bimetallic complex where intramolecular reduction of a metal alkyl group by the other, already decomposed, metal fragment is a possibility.

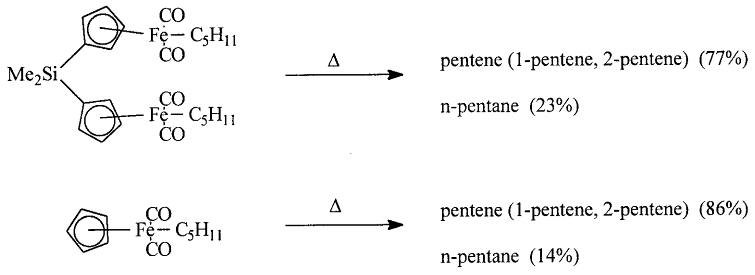


Fig. 9. Thermal decomposition of iron–alkyl complexes. The bimetallic complex yields significantly more alkane than the monometallic complex.

4.6. Formation of branched Fischer–Tropsch products

The formation of branched products in the Fischer–Tropsch synthesis has been studied by Pichler [51] and Schulz [52]. These products are almost exclusively methyl-branched, and are found only as minor components of the product distribution; linear olefins, alkanes and oxygenates being the predominantly formed products. Several proposals have been made to account for the formation of methyl-branched products. According to the proposal of Wojciechowski, a 1,2-hydrogen shift of the alkyl chain results in the formation of a 1-methyl surface alkyl species [53]. Chain growth by methylene insertion into this species followed by termination in the normal way yields the methyl-branched products (Fig. 10). Such a 1,2-hydrogen shift can be understood in terms of a reversible β-hydride elimination of the linear surface alkyl species followed by hydride addition to the terminal carbon (Fig. 10).

Reversible β-hydride elimination reactions have been widely studied in reactions of transition metal-alkyl complexes. For example, Reger and Culberson observed the formation of internal olefins and α-olefins as products of the decomposition of iron-alkyl compounds [45]. Thus $[CpFe(CO)(PPh_3)(C_4H_9)]$ decomposed upon heating to give a mixture of 1-butene, *trans* 2-butene, and *cis* 2-butene. Furthermore,

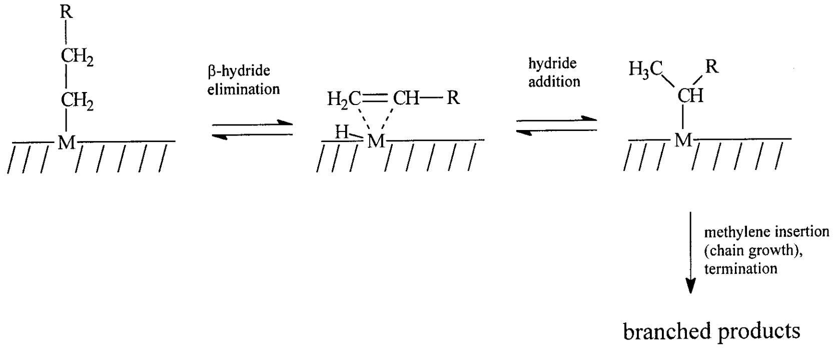


Fig. 10. Possible mechanism for the formation of methyl-branched Fischer–Tropsch products.

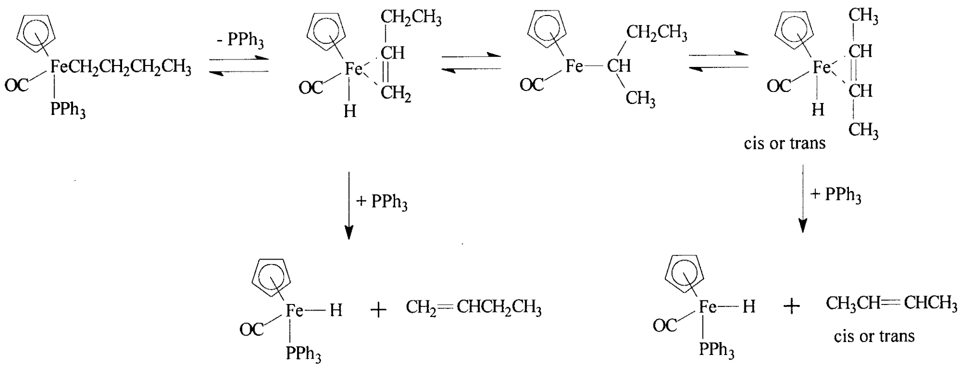


Fig. 11. Reversible β-hydride eliminations result in the isomerisation of the alkyl ligand.

when the deuterium labelled complexes [CpFe(CO)(PPh$_3$)(1,1-d$_2$-C$_4$H$_9$)] and [CpFe(CO)(PPh$_3$)(2,2-d$_2$-C$_4$H$_9$)] decomposed, complete deuterium scrambling throughout the chain of the butene products was observed. It is thus apparent that isomerisation of the alkyl chain takes place by reversible β-hydride elimination, and that under the reaction conditions many such isomerisations occur on average before dissociative β-hydride elimination gives the butene decomposition products (Fig. 11).

Methyl-branched species may also be formed as secondary products by the reabsorption of α-olefin products to form 1-methyl-branched alkyl species (c.f. Fig.

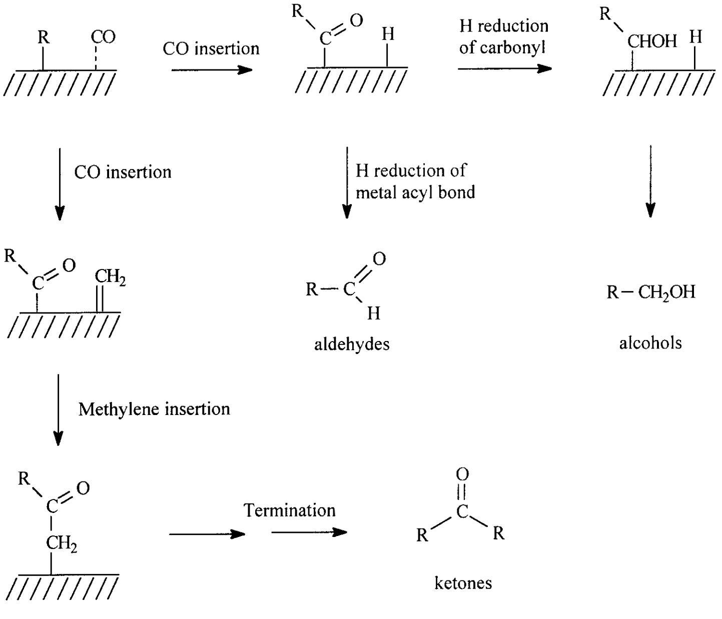


Fig. 12. Possible mechanisms for the formation of oxygenates in the Fischer–Tropsch reaction.

10). This was demonstrated by Schulz in co-feeding experiments using ^{14}C labelled olefins [54].

4.7. Carbonyl insertion: formation of oxygenates

Oxygenated compounds produced in the Fischer–Tropsch reaction include alcohols, aldehydes, acids, and ketones. The majority of the products are linear with terminal functionality. The amounts and types of oxygenates formed is highly dependent on the catalyst and the reaction conditions, but typically on an iron based catalyst ethanol is the principle oxygenate formed, followed by methanol, *n*-propanol, and acetic acid [55]. Oxygenates in the Fischer–Tropsch reaction may be formed through a CO insertion reaction with a surface alkyl species to form a surface acyl species (Fig. 12). Acyl compounds of Fischer–Tropsch active metals have been synthesised [56,57], and characteristic acyl bands have been identified by in situ IR studies [5]. Alcohols and aldehydes could then be formed as a result of the partial reduction of the acyl species by surface hydrogen [58].

5. Alkenyl mechanism for chain propagation and termination

The alkenyl mechanism (Fig. 13) has been proposed by Maitlis as an alternative to the alkyl mechanism [59]. This mechanism, like the alkyl mechanism, proposes that the Fischer–Tropsch reaction is a polymerisation of surface methylene species which are formed from the dissociative chemisorption of synthesis gas and subsequent hydrogenation of carbide on the catalyst surface. The reaction is initiated by the formation of a surface vinyl species ($-CH=CH_2$) from a surface methyne ($\equiv CH$) and a surface methylene ($=CH_2$). Chain growth is then proposed to occur through the reaction of this vinyl species with a surface methylene to form an allyl species ($-CH_2CH=CH_2$). The allyl species then undergoes isomerisation to yield an alkenyl (vinylic) species ($-CH=CHCH_3$) which may react further. Termination occurs when the surface alkenyl species is reduced by surface hydrogen to form the free alkene.

5.1. Model compounds: decomposition of rhodium μ-methylene methyl complexes

The alkenyl mechanism was initially proposed as a result of experiments on the decomposition of the rhodium complexes $[Cp^*Rh(\mu\text{-}CH_2)(CH_3)]_2$ and $[\{Cp^*Rh(\mu\text{-}CH_2)\}_2(CH_3)(MeCN)]^+$ [60,61,26]. These dinuclear complexes contain both methyl and bridging methylene species, and thus may be good model compounds for the postulated surface intermediates present in the Fischer–Tropsch reaction. The neutral dimethyl compound was decomposed either thermally at approximately 300°C or at lower temperatures (20–50°C) in the presence of a one electron oxidizer such as Na_2IrCl_6 to give methane and propene as the organic products, with smaller amounts of ethylene also formed. The cationic complex decomposed in the presence of Na_2IrCl_6 to give predominantly propene. These results appear to be consistent

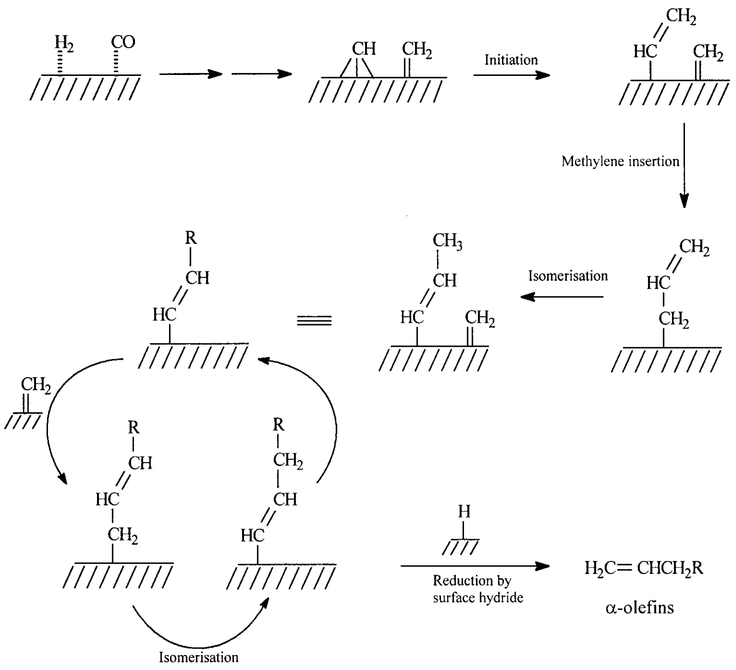


Fig. 13. The alkenyl mechanism for the Fischer–Tropsch reaction.

with the alkyl mechanism for hydrocarbon formation, involving a simple $CH_3 + CH_2 + CH_2$ coupling followed by β-hydride elimination. However, ^{13}C and deuterium labelling studies indicated otherwise. When the labelled compounds $[\{Cp^*Rh(\mu\text{-}CH_2)\}_2(CD_3)(MeCN)]^+$ and $[\{Cp^*Rh(\mu\text{-}CH_2)\}_2(^{13}CH_3)(MeCN)]^+$ were pyrolysed, the major propene isotopomers (ca. 80%) were found to be $CD_2{=}CHCDH_2$ and $^{13}CH_2{=}CHCH_3$, respectively [61]. The isotopomers expected from a $CH_3 + CH_2 + CH_2$ coupling decomposition analogous to the alkyl mechanism, $CH_2{=}CHCD_3$ and $CH_2{=}CH^{13}CH_3$ were only formed as minor products. Similar results were obtained when labelled $[Cp^*Rh(\mu\text{-}CH_2)(CH_3)]_2$ was decomposed in the presence of one-electron oxidants such as $IrCl_6^{2-}$ and Fe^{3+} [61]. A decomposition mechanism was put forward to rationalise these observations (Fig. 14). This mechanism involves the formation of a η^1-vinyl species from the methyl and one bridging methylene. This vinyl then couples with the other bridging methylene to give an η^1-allyl species. The metal hydride adds to the allyl species to form propene. This mechanism, though complicated, appears to represent a lower energy pathway than that of methylene insertion into a metal alkyl bond. The coupling of a metal-bonded sp^2 vinylic carbon with a metal-bonded sp^3 methylene carbon is favoured over coupling between metal-bonded sp^3 alkyl and methylene carbons, because of the energetically demanding reorientation of the highly directional sp^3 orbitals. This preference for sp^2–sp^3 carbon coupling over sp^3–sp^3 coupling has also been observed by other workers. Evitt and Bergman observed

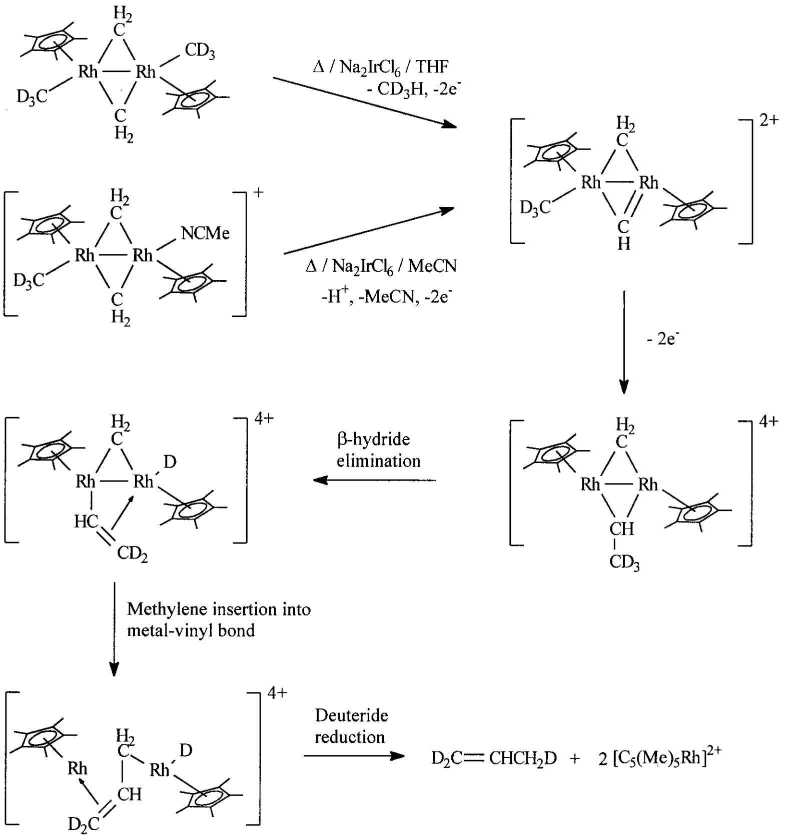


Fig. 14. Decomposition mechanism of $[Cp^*Rh(\mu\text{-}CH_2)(CD_3)]_2$ and $[\{Cp^*Rh(\mu\text{-}CH_2)\}_2(CD_3)(NCMe)]^+$.

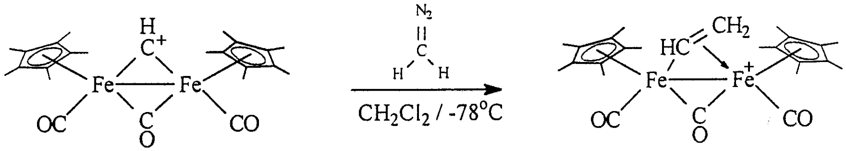
that reductive elimination in cobalt alkyl-acyl, and cobalt alkyl–vinyl complexes (sp^2–sp^3 coupling) was favoured over reductive elimination in a cobalt alkyl–alkyl complexes (sp^3–sp^3 coupling) [62]. This was attributed to the ability of the former systems to donate an extra pair of electrons to the metal centre in the elimination transition state.

On the basis of these experiments, it appears that surface vinyl/alkenyl species might be key intermediates in the Fischer–Tropsch synthesis. The interaction between these sp^2 vinyl species and the sp^3 surface methylene species would then be more favourable than an interaction between methylene and sp^3 surface alkyl groups.

5.2. Other evidence for the formation of surface alkenyl species

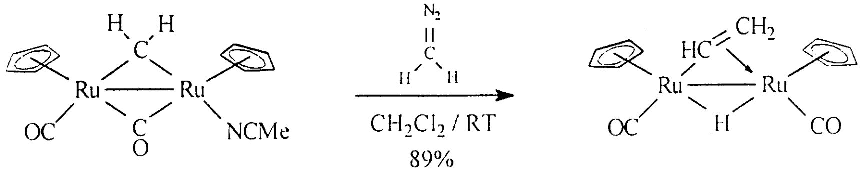
The formation of surface alkenyl species is suggested by evidence from model studies on the compound $[\{CpFeCO\}_2(\mu\text{-}CO)(\mu\text{-}CH)]PF_6$ [63]. This compound reacts readily with diazomethane at -78°C in CH_2Cl_2 to form the μ-vinyl complex

[{CpFeCO}$_2$(μ-CO)(μ-η^1,η^2-CH=CH$_2$)] PF$_6$ (Eq. (6)). This reaction models the proposed coupling of a surface methyne (≡CH) with a surface methylene to form a surface vinyl species (–CH=CH$_2$).



(6)

Akita and Knox have observed similar results on a diruthenium model complex [64]. Reaction of [Cp$_2$Ru$_2$(μ-CH$_2$)(μ-CO)(CO)(NCMe)] with diazomethane in dichloromethane at room temperature gave the alkenyl product [Cp$_2$Ru$_2$(μ-η^1,η^2-CH=CH$_2$)(μ-H)(CO)$_2$] in high yield (Eq. (7)). This provides another example of the ease with which carbon-carbon coupling may result in the formation of vinyl species from C$_1$ hydrocarbon fragments.



(7)

Surface vinyl species have also been observed in ultra-high vacuum experiments on single crystal surfaces of nickel, silver, copper and platinum [14] (although it should be noted that the last three are not Fischer–Tropsch active metals). These η^1-vinyl species have been formed by the surface decomposition of ethylene [65] and vinyl halides [66].

5.3. Evidence for the coupling of alkenyl and methylene species

The coupling of alkenyl moieties with a methylene species has been demonstrated in the decomposition of vinyl-substituted dirhodium complexes [Cp*Rh(μ-CH$_2$)(–CH=CHR)]$_2$ (R = H, Me) [67,68]. Upon heating to 330°C, [Cp*Rh(μ-CH$_2$)(–CH=CH$_2$)]$_2$ decomposes to give organic products consisting of 88% propene (Fig. 15). The same complex reacts with the single electron oxidiser Ag$^+$ in MeCN to form the η^3-allyl complex [Cp*Rh(η^3-C$_3$H$_5$)(MeCN)]$^+$ (Fig. 15). Analogous reactions occur with the dipropenyl complex [Cp*Rh(μ-CH$_2$)(–CH=CHMe)]$_2$. The product of pyrolysis at 340°C is a mixture of but-1-ene and but-2-ene, and reaction with Ag$^+$ in MeCN gives [Cp*Rh(η^3-CH$_2$CHCHMe)(MeCN)]$^+$ (Fig. 15). These products all result from a coupling between μ-CH$_2$ and the η^1-alkenyl substituent.

5.4. Evidence for the allyl to vinyl isomerisation

The isomerisation of the allyl intermediate to a surface alkenyl species that can undergo further chain growth is a key step in the proposed alkenyl mechanism. This

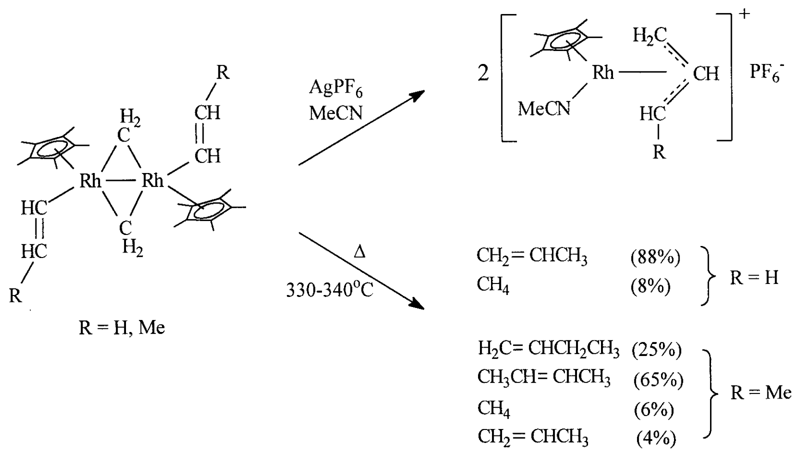


Fig. 15. Model system for the coupling of surface vinyl with surface methylene.

isomerisation, however, has little literature precedent. Recently a mechanism for the isomerisation has been proposed based on a di-iridium model system [69]. The compound $[Ir_2(CH_3)(CO)_2(\mu\text{-}RC{=}CR)(dppm)_2]^+$ (R = Me, Et; dppm = $Ph_2PCH_2PPh_2$) rearranges at ambient temperature to $[Ir_2H(CO)_2(\mu\text{-}\eta^1,\eta^3\text{-}CHC(R)C(H)R)(dppm)_2]^+$. Labelling studies indicate that this occurs by the mechanism shown in Fig. 16, where an η^3-allyl intermediate isomerises to form the vinylcarbene product. A similar mechanism for the η^1-allyl to vinyl isomerisation in the Fischer–Tropsch reaction is inferred from this evidence. The surface η^1-allyl species isomerises to form an η^3-allyl, α-hydride elimination then gives a η^1,η^3-vinylcarbene intermediate, and surface hydride transfer to the γ-carbon produces the surface alkenyl species (Fig. 16).

5.5. Incorporation of labelled vinylic probes in Fischer–Tropsch products

Maitlis and co-workers have investigated the Fischer–Tropsch mechanism further by adding labelled vinylic probe molecules to Fischer–Tropsch reactions over various catalysts. Doubly labelled vinylic probes $Si(^{13}CH{=}^{13}CH_2)_4$, $Br^{13}CH{=}^{13}CH_2$ and $^{13}CH_2{=}^{13}CH_2$ were added to $^{12}CO/H_2$ synthesis gas and passed over rhodium based [70–72] and ruthenium based [73] catalysts. The hydrocarbon products were then analysed by GC-MS to determine the level of ^{13}C incorporation. The results indicate that the amount of $^{13}C_1$- and $^{13}C_3$-incorporated hydrocarbon approximately matches the expected natural abundance percentages. However the amount of $^{13}C_2$-incorporated hydrocarbons is several orders of magnitude larger than the amount expected from ^{13}C natural abundance. It is therefore apparent that the uncleaved vinylic probes are incorporated into the chain during the Fischer–Tropsch reaction. Furthermore, the amount of incorporated ^{13}C decreases with the increasing chain length of the molecule. This implies that the vinylic probes are incorporated during the initiation, and not the propagation phase of chain building.

Statistical analysis indicates that the relative amounts of $^{13}C_2$ incorporation in different chain length hydrocarbons are consistent with a model assuming the vinyl probes are incorporated only during initiation. The propagation is facilitated exclusively by addition of surface methylene resulting from the hydrogenation of CO on the catalyst surface. Vinyl bromide acted as an efficient promoter for the reaction, increasing overall reaction rates by two to three times, without changing the product distributions of the $C_{\geq 2}$ hydrocarbons. This suggests that vinyl bromide readily forms surface vinyl by breaking the carbon-bromine bond, and that these surface vinyl species initiate chain formation in the Fischer–Tropsch synthesis. Probe incorporation from tetravinylsilane and ethylene was lower than for vinyl bromide, presumably because of reduced formation of surface vinyl from these probes.

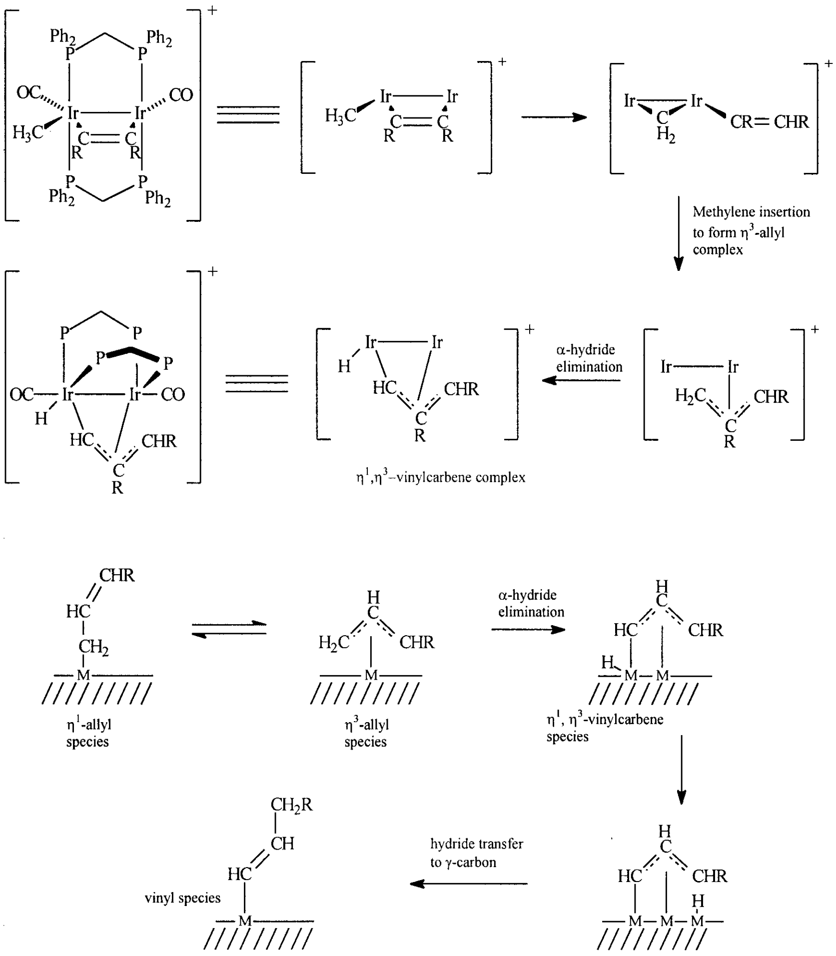


Fig. 16. Isomerisation of allyl substituent to a vinyl substituent in a model system and the inferred mechanism of this isomerisation in the Fischer–Tropsch synthesis.

When alkyl probe molecules such as $Si(^{13}CH_2^{13}CH_3)_4$ and $Br^{13}CH_2^{13}CH_3$ were added to the synthesis gas, there was no significant incorporation of $^{13}C_2$ in $C_{\geq 3}$ products [72]. Studies on single crystal surfaces of a variety of metals have established the formation of surface alkyl species from alkyl halides [14], and it would thus appear that these probe molecules do form surface ethyl species which do not however participate in Fischer–Tropsch chain growth.

Very recently, ^{13}C NMR studies have provided further evidence that vinylic probes are incorporated only during initiation [74]. $^{13}CH_2{=}^{13}CH_2$ was added to a Fischer–Tropsch synthesis reaction over a ruthenium catalyst. The synthesis was carried out under kinetic control (160°C) in order to minimise secondary reactions. Analysis of the $^{13}C_2$-incorporated hydrocarbon products indicate that the olefinic products are of the form $^{12}CH_2{=}^{13}CH{-}^{13}CH_3$ (propene), $^{12}CH_2{=}^{12}CH{-}^{13}CH_2{-}^{13}CH_3$ (1-butene) and $^{12}CH_2{=}^{12}CH{-}(^{12}CH_2)_n{-}^{13}CH_2{-}^{13}CH_3$ (higher olefins). These authors explain this result as supporting evidence that the labelled probes form surface vinyl species which initiate polymerisation of surface methylene. When the reaction was carried out at higher temperature (190°C), significant amounts of $^{13}C_1$- and $^{13}C_3$-incorporated olefins and the isotopomer $^{13}CH_2{=}^{13}CH{-}^{12}CH_3$ were observed. These products appear to result from secondary cleavage and isomerisation reactions of the primary Fischer–Tropsch olefinic products.

5.6. Formation of branched hydrocarbons

Maitlis has proposed a mechanism to account for the presence of small amounts of branched hydrocarbons in the Fischer–Tropsch product distribution [59]. In his proposal, the linear η^1-allyl intermediates ($-CH_2CH{=}CHR$) can isomerise via a η^3-species to form the branched η^1-allyl ($-CH(R)CH{=}CH_2$) species (Fig. 17). This in turn can convert to the corresponding surface alkenyl and undergo chain growth, leading to ethyl-branched hydrocarbons. The steric hindrance of the alkyl substituent on the α-chain position inhibits chain growth, thus explaining the low abundance of branched products. It should be noted however that branching which is present in the Fischer–Tropsch products is predominantly methyl branching (see Section 4.6), and that ethyl-branched products are present only as trace components of Fischer–Tropsch product distributions. The mechanism proposed by Maitlis is therefore not able to adequately explain the branching that occurs in the Fischer–Tropsch synthesis.

5.7. Formation of alkanes and oxygenates

The alkenyl mechanism has so far been used to rationalise the formation of α-olefins, and needs to be extended to include the formation of other Fischer–Tropsch products. It is thought that alkanes are a secondary product resulting from hydrogenation of the primary α-olefins. Indirect evidence for this is provided by the observation that in a kinetically controlled Fischer–Tropsch synthesis, higher flow rates caused a decrease in selectivity for alkanes and a corresponding increase in α-olefin selectivity [74].

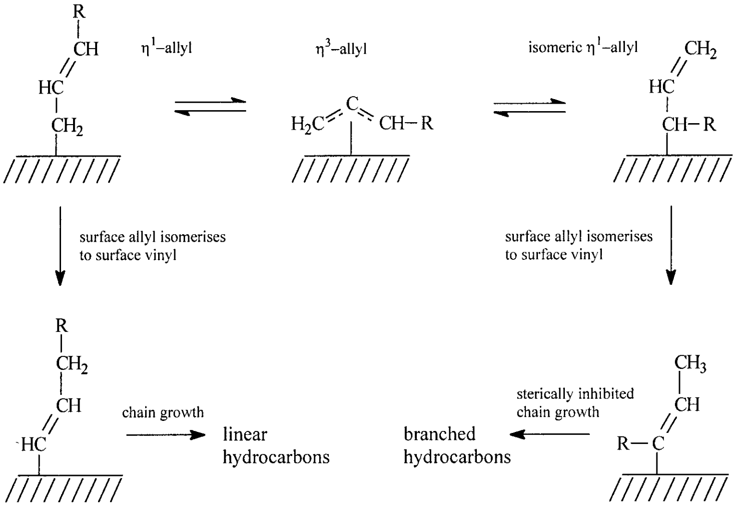


Fig. 17. Alkenyl mechanism for the formation of branched hydrocarbons.

The formation of oxygenates is particularly hard to explain in the light of the vinylic probe experiments described above. Labelled vinylic probes were not incorporated in the oxygenates during these experiments, thus implying that oxygenates are formed by a completely different mechanistic pathway.

6. Conclusions

The use of appropriate organometallic and surface science models may provide much relevant information about the mechanisms of the Fischer–Tropsch reaction, in the absence of direct observations of intermediates on catalytic surfaces. Although the reaction conditions of these organometallic and surface science systems are often vastly different from those under which industrial Fischer–Tropsch is operated, the observed chemistry of intermediate species and metal reaction sites in the model systems may be used, with caution, as a guide for deducing mechanistic principles about the heterogeneous Fischer–Tropsch reaction.

There is general agreement that the Fischer–Tropsch reaction is a polymerisation reaction of surface methylene species. However the mechanism of this polymerisation is still disputed. There are two main proposals as to how the carbon chain grows. The first proposed mechanism involves surface alkyl species as the key chain carriers. The second proposal regards surface alkenyl species as the chain carriers. There is evidence in support of both these mechanisms.

The alkyl mechanism has the advantage of being simple. The chemistry of all the key steps (methylene insertion into a metal–alkyl bond, β-hydride elimination and reduction of metal–alkyl species by hydride) is well established in organometallic solution chemistry. It is worth noting that metal–alkyl species are key intermediates in many important catalytic reactions, including hydrogenations, hydroformylations and polymerisations of α-olefins. Recently it has been discovered that complexes of the main Fischer–Tropsch-active metals i.e. Fe and Co can act as homogeneous olefin polymerisation catalysts [75]. The accepted mechanism of these polymerisation reactions involves successive insertions of the olefinic double bond into a metal–alkyl bond, not unlike the proposed insertion of methylene into the metal-alkyl bond in the Fischer–Tropsch reaction.

The relatively recently proposed alkenyl mechanism is more complicated than the alkyl mechanism. There is evidence that the sp^2–sp^3 carbon coupling involved in proposed chain propagation is kinetically favoured over the sp^3–sp^3 carbon coupling required in the alkyl mechanism. Evidence of vinylic probe inclusion in Fischer–Tropsch products also supports the alkenyl mechanism. However most of the organometallic model systems used to support the mechanism have not used common Fischer–Tropsch metals such as iron and cobalt, and the chemistry of some key steps in the mechanism is not well established. In particular the isomerisation of surface allyl species to alkenyl species has little precedent in model studies. In addition, the alkenyl mechanism cannot easily explain the presence of methyl-branched products in Fischer–Tropsch distributions. The alkenyl mechanism also cannot account for the formation of alkanes as primary products. In this mechanism, these important Fischer–Tropsch products must be regarded as secondary products resulting from the hydrogenation of primary olefinic products.

The formation of oxygenates in the Fischer–Tropsch synthesis is not particularly well explained by either mechanism, although it has been postulated that terminally functionalised oxygenates arise from carbon monoxide insertion into surface hydrocarbon species. However, further research is needed to confirm this mechanism or to provide an alternative.

The product distributions, nature of the catalyst and reaction conditions of commercial Fischer–Tropsch processes are diverse. Under a wide range of conditions, it is to be expected that many different surface species will be formed on the catalyst surface, and it is possible that there is not one mechanism operating for the formation of all observed products. Both alkyl and alkenyl intermediates may play an important role under various conditions.

The Fischer–Tropsch synthesis at present has limited commercial application because of the decline in world oil prices over the last 20 years. However world oil reserves will become depleted, and the cost of producing oil will increase as the most economically exploitable oil fields are used up. The world has large coal and natural gas reserves which will become an important source of energy if the price of oil increases, and Fischer–Tropsch processes are likely to be used to exploit these reserves. In addition, Fischer–Tropsch fuels have very low sulphur, nitrogen and aromatics content relative to conventional oil-derived fuels, and may therefore become important in efforts to meet environmental targets for noxious emissions. For example, diesel derived from Shell's Fischer–Tropsch plant in Malaysia is currently used in southern California in an effort to reduce sulphur emissions [76].

Fischer–Tropsch derived chemicals have a higher value than fuel, and the production of raw materials for the chemical industry is already an important application of Fischer–Tropsch processes. A mechanistic understanding of the Fischer–Tropsch reaction may lead to the development of technology for more selective processes. Increased selectivity for the production of high value chemicals would lead to widespread commercial applications of Fischer–Tropsch technology.

At the turn of the century, the Fischer–Tropsch process must be considered a mature industrial technology, however, as illustrated in this review, many fundamental questions concerning the mechanism remain unanswered. Research into fundamental Fischer–Tropsch chemistry is therefore likely to be extremely valuable in the future as commercial Fischer–Tropsch processes become increasingly important.

Acknowledgements

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