

Fischer–Tropsch, organometallics, and other friends

Peter M. Maitlis *

Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK

Received 5 April 2004; accepted 21 May 2004

Available online 31 July 2004

Abstract

Recent researches on the mechanism of the Fischer–Tropsch hydrogenation of CO *heterogeneously* catalyzed by ruthenium, rhodium, cobalt or iron (on silica), both with and without added probe molecules, are reviewed. When the reactions are carried out under *mild conditions* of temperature, pressure and catalyst, we find that, although the absolute activities of the four catalysts differ, the relative product distributions are rather similar. Our data indicate that the primary products are largely *n*-1-alkenes (and methane); *n*-alkanes and some internal olefins are also produced, but these arise substantially from subsequent (secondary) reactions of the 1-alkenes. Mechanisms for the formation of 1-alkenes are suggested, both from our work and that of other groups, based upon data from (i) a variety of labeling and spectroscopic studies, (ii) model stoichiometric reactions of organometallic complexes, and (iii) some theoretical and computational data now available. The mechanism in best agreement with experimental data involves, (a) initiation via deoxygenation of coordinated CO and the production of a C₂ based surface species, probably a vinyl {CH₂=CH_(ad)}, via formation of surface carbide, methylidyne and methylene; (b) propagation by reaction of surface methylene {CH_{2(ad)}} with surface vinyl or alkenyl {RCH=CH_(ad)} to give a surface allyl {RCH=CHCH_{2(ad)}}, followed by a 1,3-H shift to generate a new surface alkenyl {RCH₂CH=CH_(ad)}; and (c) termination by hydride-mediated cleavage of the alkenyl chain from the catalyst giving the 1-alkene, RCH₂CH=CH₂, directly. By contrast, the hydrogenation of CO homogeneously catalyzed by soluble complexes (chiefly of Ru) is reported to occur only under more stringent conditions and to lead mainly to methanol and ethylene glycol; clearly quite different mechanisms operate there.

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Keywords: Fischer–Tropsch; CO hydrogenation; Alkene formation; Mechanisms; Organometallic intermediates

1. Autobiographical introduction

As this is a personal view, I will begin with some personal history. I also want to introduce the reader to some of my friends and colleagues; especially Roly Pettit¹ as we influenced each other in a somewhat symbiotic relationship for several years and because he was very influential in organizing an organometallic understanding of Fischer–Tropsch.

I started my doctoral researches (on a mechanistic organic theme of electrophilic substitution in heterocycles) in 1953 in the laboratories of Michael Dewar,² a brilliant organic chemist who worked at what was then Queen Mary College of the University of London. Michael was a theoretician but he encouraged his students and coworkers to carry out experiments, as he wanted to see if the Molecular Orbital theories he had developed did indeed work. He was also the first to explain the metal–olefin bonding in ethene–Ag⁺ (and in Zeise's salt), but sadly he never pursued this theme. An early recruit to his group was Roly Pettit, a young postdoc from

* Tel.: +44-114-222-9320; fax: +44-114-222-9346.

E-mail address: p.maitlis@sheffield.ac.uk.

¹ Professor Rowland Pettit, 1927–1981; we called him “Roly” but in the USA he was “Rolly”.

² Professor M.J.S. Dewar, 1918–1997.

Australia, who came as an 1851 Exhibitioner after finishing his PhD with Badger in Adelaide. He was the prototypic Australian: big, muscular, very energetic, and outspoken with a fund of aphorisms and witty slang; on occasion, in his impatience to start an experiment, he would not wait for Eddie, our lab-boy, to bring the nitrogen up by the goods hoist, but charged up several flights of stairs to our lab with a tank of gas on his shoulder. He was also a heavy smoker and enjoyed the occasional beer too. But above all Roly was a superb experimental chemist. We worked next to each other for several years and shared many common frustrations: the facilities were poor; we had little or no equipment; worst of all, sometimes the experiments did not work! As it was well before Health and Safety at Work rules, we practised what might be called “macho” chemistry: rather than read up on the experiment, and first take the necessary precautions, we would dive in – with interesting consequences. Since our fume hoods were useless, our lab was often shrouded in a choking smog reminiscent of a Sherlock Holmes story of Limehouse. Indeed, at one time hardly a month went by without one or other of us being escorted to the casualty department of the Mile End Hospital, conveniently situated next door to Chemistry. Roly’s task was to see if he could make tropylium, $C_7H_7^+$. Eventually he succeeded but only after several explosions and many heartbreaking disappointments; even then, it turned out that several others had beaten him to that prize.

In the late 1950s the Dewar group at QMC slowly wound down: Michael and Roly went to the USA, first to Chicago and then to Texas. I also crossed the Atlantic (in 1961) to learn organometallic chemistry with Gordon Stone at Harvard and then, later, to start my own research group at McMaster University in Hamilton, Ontario, Canada. During this period my work had moved from organic mechanisms via organo-boron chemistry (at QMC) to metal promoted acetylene oligomerization, following some studies by Malatesta’s group in Milan, and on tetraphenylcyclobutadiene-palladium complexes [1]. My research interests became focused on the effects of metals on organic molecules, a theme that has fascinated me ever since.

Roly had also started to work in organometallic chemistry and came along to hear a talk I gave at the Washington ACS meeting in March 1962 on tetraphenylcyclobutadiene-palladium chemistry. That possibly sparked his interest in this area and he then went on to develop the very elegant chemistry of complexes of cyclobutadiene itself and synthesised the ground-breaking cyclobutadiene-iron tricarbonyl [2]. He made many other novel organometallic molecules and then started applying organometallic concepts to reactivity where he proposed, in the late 1970s, important contributions to our understanding of the heterogeneously catalyzed Fischer–Tropsch reaction [3].

In 1972, after ten years in Canada, I recrossed the Atlantic to take up the Chair of Inorganic Chemistry at Sheffield University. I had been very fortunate at McMaster University and had managed to avoid most administrative chores but, just months after arriving back in England, and as my other colleagues were keen to pass on the honour, I was “selected” to be Head of Department. The next few years were very full and exciting, and I experienced a very steep learning curve in how science is managed, especially in respect of one or two of my senior colleagues. I determined to do the administration effectively but to ensure that I still had time for research, which was, after all, the reason I had been appointed in Sheffield. I also felt that part of my remit was further to popularize organometallic chemistry. With this aim, Bernard Shaw in Leeds, and Jon McCleverty, Ron Mason and I, in Sheffield, organized a series of Sheffield–Leeds Symposia on Organometallic and Inorganic Chemistry during the 1970s and early 1980s. They soon became regarded as the highpoints of each years’ conference circuits on organometallic chemistry.

My own work developed from the chemistry of palladium and of metal complexes derived from acetylenes to pentamethylcyclopentadienyl–rhodium and –iridium complexes; these promoted catalyses, involving C–H and C–C formation and cleavage, and my group spent a happy couple of years unraveling the mechanisms by which those reactions proceeded. That in turn led to our investigations of homogeneously catalyzed carbonylations, which, later, led to our work on heterogeneously catalyzed carbonylations and the Fischer–Tropsch process.

2. Fischer–Tropsch reactions

Some 80 years ago Fischer and Tropsch discovered that a mixture of higher hydrocarbons was formed when hydrogen and CO were passed over Fe or Co oxides at one atmosphere pressure and temperatures in the range 250–300 °C [4]. At higher temperatures methane became the sole product; methane was also the sole product when CO was hydrogenated over nickel [5]. The description “Fischer–Tropsch” was quickly extended to cover all products (hydrocarbons and oxygenates) from the metal catalyzed hydrogenation of CO under a wide variety of conditions of catalyst, pressure and temperature. The term today can even include “gas to liquids” technology.

Initially the process was used to make liquid fuels (petrol = gasoline) from coal via primary gasification to syngas ($CO + H_2$). More recently it has been used to produce higher value specialty chemicals via *n*-1-alkenes made from syngas derived from natural gas (methane) or coal.

Although the formation of hydrocarbons is thermodynamically favorable (for example, for propene, $2\text{H}_2 + 1\text{CO} = \text{H}_2\text{O} + 1/3(\text{C}_3\text{H}_6)$, $\Delta G_{(227^\circ\text{C})}^0 - 96 \text{ kJ/mol}$) it does not occur in the absence of catalysts because CO is kinetically inert and no simple paths are available. One reason may be that the formation of partly hydrogenated lower oxygenates that might be intermediate in such reactions is thermodynamically unfavorable,

e.g. for methanol, $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$,

$$\Delta G_{(227^\circ\text{C})}^0 + 27 \text{ kJ/mol};$$

and for formaldehyde, $\text{H}_2 + \text{CO} = \text{HCHO}$,

$$\Delta G_{(227^\circ\text{C})}^0 + 51 \text{ kJ/mol}.$$

The classic catalysts for CO hydrogenation are metallic Fe, Co, Ni, Ru or Rh supported on various oxides. However other metals (such copper) and many different supports are also used. The wide range of conditions brings with it a wide range of products, including linear and branched chain hydrocarbons (alkanes and alkenes), as well as some cyclic ones, oxygenates (such as methanol, ethanol and some higher alcohols), and even occasional anomalies such as amines. Many hundreds of patents have been taken out on aspects of the process especially in attempts to make the reaction more selective, and these list many ways to make and tune the catalysts (involving different promoters and supports) in addition to the actual active metals [6].

By definition, metal–carbon bonds, and hence organometallic species, must be involved in reactions between metals and such simple organic molecules. The unusual nature of the primary step in which CO is converted into simple hydrocarbons on metal particles tempted researchers to investigate the process and organometallic chemists devoted much effort to modelling the process and the species which were believed to be involved. Many hundreds of papers (and proposals for research funding!) have been written on the theme, from a variety of viewpoints: there were those who believed that only polymetallic cluster complexes could model the reactions that occurred in the catalytic system; there were those who believed the exact contrary, that there was no need to invoke clusters as all the essential steps could be demonstrated on complexes with only one or two metal centers. And there were even those who believed that the metal surface was so unique that no molecular models were possible.

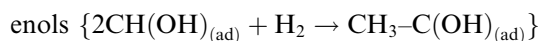
A major complication in discussing the science underlying Fischer–Tropsch is that it is composed of several quite separate reaction sequences. These include the primary hydrogenation of CO (giving *n*-alkenes, methane, and some *n*-alkanes), and the many subsequent reactions undergone by these primary organic products, including hydrogenation, hydrogen migration, skeletal isomerization, cyclization, and sometimes even dehydrogenation and oxidation.

Much of the focus of attention of *chemical* research on the Fischer–Tropsch reaction has been on the primary steps; by contrast, studies in *engineering* have concentrated more on the overall product distribution and hence on the secondary reactions.

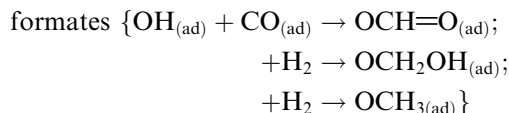
As we (together with many others) have shown that 1-alkenes are the primary products, the term “Fischer–Tropsch” will be used here in the narrow sense to refer to those CO hydrogenation reactions heterogeneously catalyzed by Fe, Co, Ru, or Rh which give largely α -olefins [7,8]. Hypotheses that have been put forward to explain the products formed from the Fischer–Tropsch reaction and, later, to account for the labeling found from the appropriate experiments, have been reviewed in some detail [8], and the reader is invited to consult them for further information. Some comments on the homogeneous reactions are given at the end.

3. Roly Pettit's Fischer–Tropsch mechanisms

In 1979 we invited Roly to lecture on his Fischer–Tropsch related work at our Tenth Sheffield–Leeds Symposium. Mechanisms popular at that time involved surface species such as,



and



Roly presented evidence for a scheme (Fig. 1) involving the polymerization of carbene surface species which was consistent with his labelling studies [3]. This model, which reverted to ideas that Fischer and Tropsch had originally proposed, suitably modified to take into account current theories of bonding and reactivity, became very popular and triggered major research initiatives among synthetic organometallic chemists.

Some examples of the approaches that were used to mimic the direct (stoichiometric) reduction of coordinated CO in a metal complex [9–12] include $(\text{Cp}^*)_2\text{Zr}(\text{CO})_2 + 2\text{H}_2/110^\circ\text{C} \rightarrow (\text{Cp}^*)_2\text{Zr}(\text{H})(\text{OMe})$ [9], followed by hydrolysis to methanol; and $[\text{CpFe}(\text{CO})(\text{PMe}_3)\text{Me}] + \text{successive } (\text{CO}; \text{BH}_3) \rightarrow [(\text{Cp})\text{Fe}(\text{CO})(\text{PMe}_3)(\text{COBu})^n]$ which on oxidation yielded pentanoic acid [10].³

³ Cp = $\eta^5\text{-C}_5\text{H}_5$; Cp* = $\eta^5\text{-C}_5\text{Me}_5$.

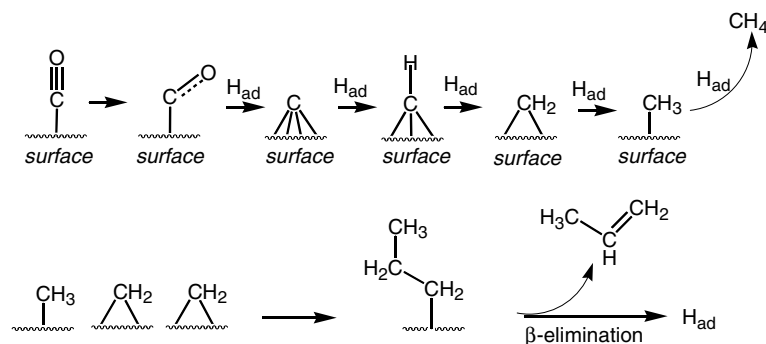


Fig. 1. Top: schematic of the activation and stepwise hydrogenation of CO, giving sequentially surface carbide, methylidyne, methylene, and methyl. Bottom: the Pettit *alkyl* mechanism involving the oligomerization of surface methylenes initiated by surface H (or methyl) and the β-elimination of propene from the surface alkyl.

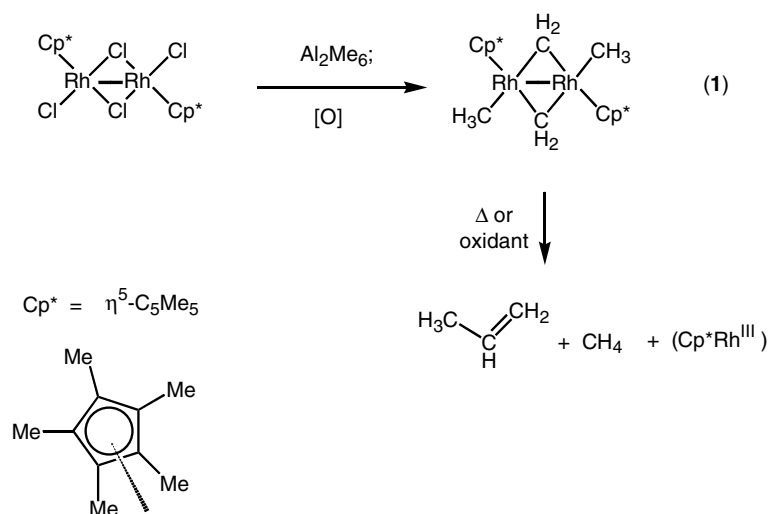


Fig. 2. The synthesis of $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CH}_2)(\text{CH}_3)\}_2]$ complex (1) and its decomposition to give propene and methane.

4. Sheffield experimental work using labelled probes

Our group in Sheffield also became heavily involved in modeling steps in the Fischer–Tropsch reactions. Kiyoshi Isobe, a most talented Japanese Postdoctoral Fellow, joined us in 1980 to develop further the basic chemistry of pentamethylcyclopentadienylrhodium complexes. He reacted $[\{\text{Cp}^*\text{RhCl}_2\}_2]$ with methyl-lithium and other alkylating agents. Not only did the reactions work, but he isolated some spectacular new types of complexes from them [13]; perhaps the most interesting was one which was characterized as the dinuclear dimethyl-bis-μ-methylene (1). In this one single molecule, containing two methyls and two methylenes bridging two metal atoms, we had the epitome of the Pettit model for the Fischer–Tropsch reaction. And Kiyoshi showed, with Isabel Saez and Andy Nutton, that it did indeed decompose, thermally or under oxidative conditions, to give propene and methane (Fig. 2).

However Isabel showed, in further elegant experiments on D- and ¹³C-labeled (1) and analogs, that the labels found in the propene were not consistent with a simple CH₃ + CH₂ + CH₂ oligomerization process. Thus the basic Pettit–Fischer–Tropsch mechanism needed some adjustment.

The question was, how should the proposed reaction schemes be modified and above all, what experiments did we have to do to check them. In fact the path before us was obvious, though difficult to negotiate. Rather than just model, we needed to do some *real* heterogeneous catalyses to develop our hypotheses in an organized manner. Which is easier said than done since, when one comes from synthetic organometallic chemistry or homogeneous metal catalyzed reactions, a complete change of one's frame of reference is necessary to devise and make sense of heterogeneous catalysis experiments. To explain the problem one can use a metaphor from art. If one compares the two pictures of young women,



Fig. 3. Two pictures illustrating the well-defined (naturalistic) and the more indefinite (impressionistic) styles in painting. Left: Domenico Ghirlandaio “Portrait of a young girl” Gulbenkian Museum, Lisbon. Right: Claude Monet “Young girls in a rowing boat” National Museum of Western Art, Tokyo.

the naturalistic Ghirlandaio⁴ and the impressionistic Monet⁵ illustrated in Fig. 3, both are outstanding expressions of pictorial art but, while the Ghirlandaio girl is clearly defined and easy to appreciate, the figures in the Monet are quite indistinct and the detail is not directly seen but needs to be inferred.

Analogously, heterogeneously catalyzed reactions are very complex and their results and interpretation are not immediately obvious, especially when the reactions are carried out on a laboratory scale. Many subtle factors need to be taken into account: not only the catalyst and the support and the conditions of the experiment, but also the methods used to prepare the catalyst and the changes in its morphology can be critical.

Thus to take our first steps in heterogeneous catalysis we needed some help and guidance. This was initially provided by Ma Futai, Professor in the heterogeneous catalysis group at the University of Hangzhou in China. Futai was a skilled and amiable older gentleman, with considerable experience in making supported metal catalysts, who spent a year in Sheffield in 1989 teaching us this gentle art. Our first work on this topic was carried out by Mike Turner (Royal Society University Research Fellow) who led our efforts, Helen Long, an excellent PhD student, and Peter Byers, who joined us as an enthusiastic postdoc from Tasmania. They studied the reactions of carbon monoxide and hydrogen, with labelled probe molecules, over rhodium and ruthenium catalysts [14,15]. Over the next few years a very talented interna-

tional group worked on the project, including Ruhksana Quyoun (who came from the University of Salford), Zhi-Qiang Wang (Dalian, China), Nyoman Marsih (Bali, Indonesia), Ryszard Kunicki (Warsaw, Poland); later we had much help and advice from Jan Kašpar and Mauro Graziani from the Trieste Heterogeneous Catalysis Group in Italy. Their work ensured that we got good and reproducible results and allowed us to expand our ideas.

We carried out both “real” Fischer–Tropsch experiments on supported metals and also more organometallic model studies. Since direct observations to see just what happens on supported metal particles under Fischer–Tropsch conditions (syngas at 150–200 °C) are not really feasible, we opted for an indirect, kinetic approach. We used a labeling technique in which we passed over the catalyst syngas together with small amounts of a doubly-¹³C labeled probe molecule (mostly ¹³C₂H₄, but the first experiments used ¹³C₂H₃Br). The products were then collected and analyzed to see where the labels appeared and from the data we could work back and deduce how they had got there. We started with rhodium on silica to match our organometallic model studies, even though this was not the best Fischer–Tropsch catalyst. Later we expanded to ruthenium, iron and cobalt catalysts (all on silica) – which were more active than the rhodium. To our surprise we found that, so long as we kept to “mild” conditions of temperature, pressure, and catalyst loading,⁶ the relative product distributions were quite similar (Fig. 4), even though the absolute ac-

⁴ Domenico Ghirlandaio “Portrait of a Young Girl” Gulbenkian Museum, Lisbon.

⁵ Claude Monet “Young Girls in a Rowing Boat” National Museum of Western Art, Tokyo.

⁶ CO:H₂ 1:1; 1 atm pressure and the lowest temperature needed to obtain useful amounts of products: Ru/150 °C, Co/180 °C, Rh/190 °C, and Fe/220 °C.

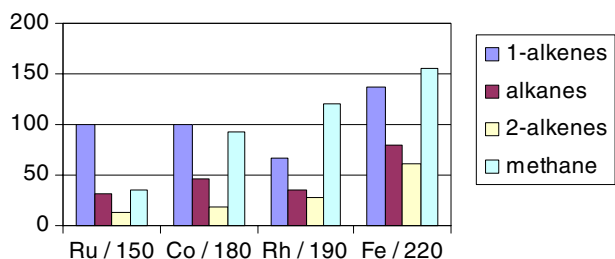


Fig. 4. Catalyst activities (product formation rates; $\mu\text{mol/g/h}$) found for CO hydrogenation under mild conditions (Ru/150 °C, Co/180 °C, Rh/190 °C, and Fe/220 °C – all on silica; CO:H₂ 1:1; 1 atm) before probe addition.

tivities of the catalysts differed substantially. We characterized the products by GC and then analyzed each individual component by mass-spectrometry to elucidate how many ¹³C labels were in the products.

More recently, Mike Turner and Nyoman Marsih, with the help of Brian Mann and Brian Taylor, found that the ¹³C NMR spectra, even of crude Fischer–Tropsch product mixtures, could be resolved to give much more detailed information [8]. These measurements allowed us to define exactly where the labels were in each product molecule and to determine whether the probe molecule had been incorporated as a C₂-unit or had been split into C₁ fragments. We also found that adding ¹³C₂H₄ probes to the syngas did not significantly perturb the basic reaction. In other words, we now had a technique that allowed us to “see” what was really happening in the Fischer–Tropsch reaction.

Other workers in the field had similar ideas and developed alternative strategies, such as the *isotope transient* experiments in which ¹²CO and ¹³CO feeds were alternated over the catalysts [16]; the appearance of ¹³C in the products was measured, and the data interpreted in terms of model schemes. A particularly important result from this work, obtained by several groups, was that C₂ species appeared to be intimately involved in the initiation [16].

Our work with ¹³C₂ probes, the isotope transient experiments, as well as the decomposition of model compounds such as (1) all led to very similar conclusions which now form the basis of any discussion of the mechanism. They indicated that the Pettit view of a surface polymerization initiated by hydride (or methyl, Fig. 1) and carried by surface methylenes was probably too simple. Furthermore theoreticians are now quite united in their calculations which indicate that metal-mediated direct Csp³–Csp³ bond forming reactions are unlikely as they are very high energy processes [17]. If, as is probable, the methylene bridges two metal atoms in the surface, the methylene carbon is sp³ hybridized, which means that the Pettit alkyl polymerization would require sp³ carbons to join with each other. Thus an alternative

is needed. This has led to our modification of the mechanism, and to even more radical suggestions by others.

5. Sheffield mechanistic arguments: the alkenyl mechanism

Our data [15] show that, while the absolute activities varied with metal and temperature, the four Fischer–Tropsch-active metal catalysts (Fe, Co, Ru, and Rh on silica) used gave basically similar product distributions of linear alkenes, alkanes, and methane from CO hydrogenation when the reaction was carried out under *mild conditions*. When we added ethene-¹³C₂ probes the NMR spectra of the 1-alkene products showed that two ¹³C atoms were incorporated and were generally adjacent at the alkyl ends (¹³CH₃¹³CH₂(CH₂)_nCH=CH₂). The *n*-alkanes and internal alkenes bore similar labels. By contrast we found rather little incorporation of ¹³C₁ into the products from our ethene-¹³C₂ probe; in other words, C–C cleavage was minimal under these conditions, though it became significant at higher temperatures. We interpret this to confirm that under the “mild” conditions the products from the primary steps are maximized and those from subsequent, secondary, reactions substantially reduced. The results showed that 1-alkenes predominated, but alkanes became more significant among the higher hydrocarbons, while internal olefins (chiefly 2-alkenes) were generally minor products. Methane was often the major single product and its product formation rate was closely dependent on the reaction temperature. Ru was generally the most active catalyst; however, Co also had high activity for 1-alkene formation. Further analysis of the data confirmed that secondary reactions were involved in the formation of alkanes and 2-alkenes.

Our experimental data lead to a picture for the mechanism of the Fischer–Tropsch reaction in the absence of added probe, involving three basic steps: (i) initiation, (ii) propagation and (iii) termination.

(i) Dihydrogen (H₂) is activated forming metal hydrides on the metal surfaces, H₂ (gas) + 2M \rightleftharpoons 2M–H. In a series of stepwise processes CO, activated (Fig. 5) by coordination to a metal atom (or atoms), is deoxygenated with the help of surface hydrogen (hydride, H_(ad)) giving water and a series of C_{1(ad)} (surface-bound) species including carbide (>C<_(ad)), methylidyne (H–C \equiv _(ad)), methylene (H₂C<_(ad)), methyl (H₃C–_(ad)) and eventually ending in the release of gaseous methane (CH₄). That these steps occur on metal surfaces is now well documented: some organometallic models are known [15], but more work is needed to establish more general patterns. However, we do not regard any of these C_{1(ad)} species as the actual initiator of a polymerization, as the experimental evidence now points to that initiation being by a C_{2(ad)} surface species, which we propose to be a vinyl (CH₂=CH–_(ad)) or a vinylidene

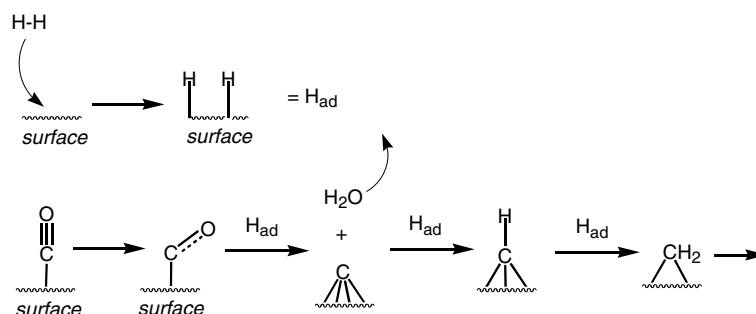


Fig. 5. Proposed first steps of the initiation of the Fischer–Tropsch mechanism: activation of H_2 to give surface hydrides, and of CO to give surface carbide, followed by stepwise hydrogenation to give methylidyne and methylene, building blocks for the next stages.

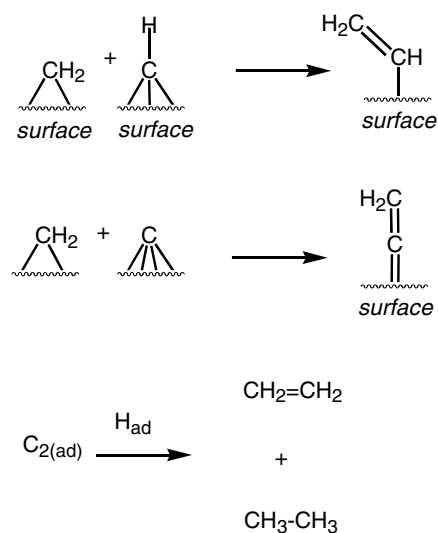


Fig. 6. Possible routes for the formation of the C_2 "active initiator" species: surface vinyl from methylidyne and methylene or surface vinylidene from carbide plus methylene.

($\text{CH}_2=\text{C}=\text{(ad)}$). Possible routes to such species are from dicarbides (which, at least for ruthenium, can be formed on heating a carbonyl), or by combination of two $\text{C}_{1(\text{ad})}$ surface species, for example, a methylidyne and a methylene (Fig. 6).⁷ The formation of the trimetallic alkenyl complex $[(\text{RCH}=\text{CH})\{\text{CpRu}(\text{CO})\}_2\{\text{WCp}\}]$ by combination of a μ -methylene diruthenium and an alkylidyne-tungsten complex [18] is a model (albeit somewhat distant) for this.

(ii) We suggest that the carriers of the polymerization chains are surface alkenyl (rather than alkyl) species which react with surface methylenes ($>\text{CH}_{2(\text{ad})}$) as shown in Fig. 7. Thus the propagation is by the coupling of an sp^2 (alkenyl carbon) with an sp^3 (methylene carbon) which is energetically a much easier process than an sp^3 – sp^3 coupling. However in order to regenerate an sp^2 carbon which can react further with $\{\text{CH}_2<_{(\text{ad})}\}$

to start the coupling cycle over again, this step now has to be followed by a H-migration to convert the first formed surface-allyl $\{\text{CH}_2=\text{CH}-\text{CH}_{2(\text{ad})}\}$ into the more reactive propenyl $\{\text{CH}_3\text{CH}=\text{CH}_{(\text{ad})}\}$. Although this step is unusual, there are now several examples of such H-migrations in organometallic chemistry [8], and we suggest it to occur during the propagation step of the polymerization.

(iii) The final, termination, step postulated by the Pettit alkyl mechanism is a β -elimination of the 1-alkene product and the regeneration of a surface hydride. β -Eliminations are well-known in organometallic chemistry and are reversible, $\text{RCH}_2\text{CH}_2-\text{M} \rightleftharpoons \text{RCH}=\text{CH}_2 + \text{M}-\text{H}$ (surface $\text{M}-\text{H}$; $\text{H}_{(\text{ad})}$). In the presence of large amounts of hydrogen the surface will be covered in hydride and hence the equilibrium will be strongly to the left and the β -elimination disfavored. This is very likely to be the situation under the operating conditions of the Fischer–Tropsch process and thus an alternative termination should be sought.

The preferred termination step in the alkenyl mechanism involves the liberation of the alkene from the alkenyl, $\text{RCH}=\text{CH}_{(\text{ad})}$ chain carrier, by reaction with surface hydride ($\text{RCH}=\text{CH}_{(\text{ad})} + \text{H}_{(\text{ad})} \rightleftharpoons \text{RCH}=\text{CH}_2$; $2\text{M} + \text{H}_2 \rightleftharpoons 2 \text{H}_{(\text{ad})}$) or, just possibly, by direct reaction with dihydrogen.

The overall alkenyl scheme proposed is therefore in good agreement with known organometallic chemistry and with the experimental findings both relating to the distribution of isotopic labels in the actual heterogeneous catalysis and the results of a variety of model systems [19]. The absence of direct $\text{C}(\text{sp}^3)$ – $\text{C}(\text{sp}^3)$ couplings is also in good agreement with the requirements of theoretical calculations.

However while the first surface C_1 starts the polymerization in the alkyl mechanism, the first, and probably rate determining, step in the alkenyl mechanism is the formation of a surface C_2 species (see also [16,20]). This is not needed if a C_2 probe molecule has been added and explains why the initiation of Fischer–Tropsch by C_2 species such as ethene is so effective.

⁷ Or possibly even $\text{C} + \text{CH}$ forming $\text{CCH}_{(\text{ad})}$ which is then further hydrogenated [17d].

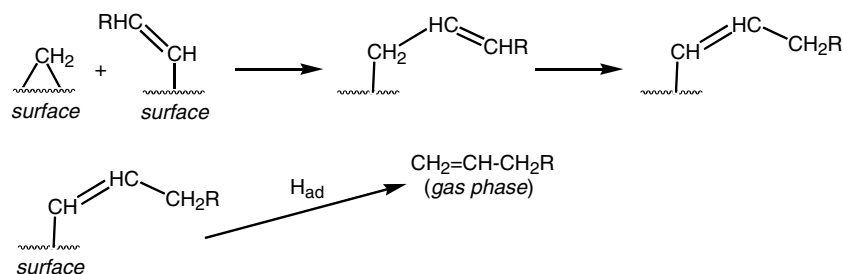


Fig. 7. Proposed Fischer–Tropsch propagation (methylene plus alkenyl followed by a 1,3-H migration) (top) and termination (alkenyl plus surface hydride) (bottom).

6. Other recently proposed mechanisms

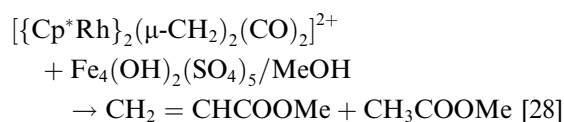
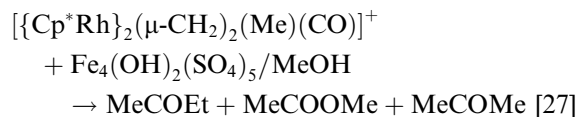
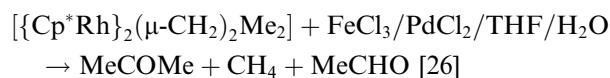
A plethora of mechanistic possibilities has been suggested. The chemically more straightforward have already been analyzed in some detail [8] and found to conflict with experimental data. A further concept in which the adding monomer is not methylene $\{\text{CH}_2\langle_{\text{(ad)}}\}$, but methylidyne $\{\text{HC}\equiv_{\text{(ad)}}\}$ followed by hydride, has quite recently been added to the theories of Fischer–Tropsch reactivity by Ciobica and van Santen [21]. This alkylidene $_{\text{(ad)}} + \{\text{CH}_{\text{(ad)}} + \text{H}_{\text{(ad)}}\}$ path explains the product distribution and some of the isotope data. A somewhat related carbide plus methylidyne mechanism followed by hydrogenation $\{\text{CH}_{\text{(ad)}} + \text{C}_{\text{(ad)}} + n\text{H}_{\text{(ad)}}\}$ has also been suggested recently based on observations of stable surface species [17d]. We must discount these ideas as the more subtle isotopic data, for example the observation of the formation of different propene isotopomers, $^{13}\text{CH}_2=^{13}\text{CHCH}_3$ and $\text{CH}_2=^{13}\text{CH}^{13}\text{CH}_3$, cannot be understood if the chain propagating steps involve direct reactions of the hydrocarbon chain with surface carbide $\text{C}_{\text{(ad)}}$ or methylidyne $\text{CH}_{\text{(ad)}}$ species; however the initiating C_2 species may be formed by such reactions.

7. “Homogeneous Fischer–Tropsch” and the direct formation of oxygenates

There has been much interest in the development of homogeneous Fischer–Tropsch catalyst systems using soluble complexes of Fe, Co, Ru, and Rh, with various promoters. No significant amounts of hydrocarbons are obtained but some C_1 and C_2 oxygenates are formed, though only under quite stringent conditions ($\geq 230^\circ\text{C}$, ≥ 400 atm pressure $\text{CO} + \text{H}_2$). Several regimes have been described including, an ionic liquid based system of Ru-chloride plus acetate and quaternary phosphonium halides in acetic acid [22]; a Rh-promoted Ru catalyst, with added cations and bases, also in acetic acid [23]; and an iodide promoted Ru system in highly polar solvents such as sulfolane, or NMP [24]. The last was

shown to contain $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ after reaction. The products are chiefly methanol and ethylene glycol, though some higher alcohols are formed in secondary reactions. Formation of methanol and ethylene glycol from CO would involve hydrogenation of the C–O bond rather than its cleavage and, as mentioned above, such processes are thermodynamically quite unfavorable and can only take place under forcing conditions with particular catalysts. The need for special (polar) solvents and the isolation of anionic ruthenium complexes from the homogeneous catalyses suggests that anionic intermediates may be involved. Thus there is little reason to expect direct homogeneous analogs of the heterogeneous reactions. Various possible schemes (via formaldehyde; or formate intermediates) to methanol and ethylene glycol have been considered but decisive evidence is lacking.

From a commercial point of view direct C_1 -based syntheses of long chain oxygenates (alcohols or carboxylic acids for use as surfactants) are desirable as such compounds have high value. So far, despite attempts to combine for example hydroformylation and Fischer–Tropsch catalysis [25], there have been no spectacular successes. We have shown from organometallic model systems based on complex (1) that a number of interesting oxygenates can be made by the oxidative coupling of C_1 entities, for example,



Such stoichiometric reactions suggest possible catalytic processes and offer a challenge to chemists and engineers.

Acknowledgement

I thank The Leverhulme Trust for a Research Award, and Mike Turner and Gian-Paolo Chiusoli for helpful comments on the manuscript. This article for the 40th Anniversary issue of the Journal of Organometallic Chemistry is dedicated to the memory of Roly Pettit, a brilliant chemist and a splendid colleague from whom I learnt a great deal.

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