The Alkenyl Mechanism for Fischer–Tropsch Surface Methylene Polymerisation; the Reactions of Vinylic Probes with CO/H_2 over Rhodium Catalysts

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Abstract: Results consistent with the participation of vinyls in the initiation and of alkenyl species in the propagation steps of the Fischer–Tropsch reaction are reported. Substantial incorporation of $^{13}C_2$ into the alkene and alkane (C_3–C_7) hydrocarbon products occurred when doubly labelled vinyls ($^{13}C_2H_3Br$, $(^{13}C_2H_3)_4Si$, or $^{13}C_2H_4$) were added as molecular probes to the hydrogenation of carbon monoxide over rhodium/ceria/silica catalysts (1 atm, 220 °C). There was, by contrast, no significant incorporation of $^{13}C_1$ into any of the organic products; thus cleavage of the C_2 probe did not occur. The degree of $^{13}C_2$ incorporation decreased with increasing molecular mass of the hydrocarbon; this indicates that the probe molecule initiated but did not propagate. A mathematical model based on polymerisation of surface methylenes initiated by a vinyl, propagated by alkenyls and terminated by reaction with a surface hydrogen or by coupling has been developed to explain the $^{13}C_2$ incorporation data. Under the conditions of the experiments, the relative ability of the probes to initiate is: vinyl bromide (60%) > tetravinylsilane (30%) > ethene (15%). Substantial formation of $^{13}C_4$ products also occurred when vinyl bromide or tetravinylsilane were used as probes; this arises from a dimerisation of the vinyl on the surface, a process which has been modelled in homogeneous systems and also by other workers in studies on single crystal surfaces. There was no significant ^{13}C incorporation into the oxygenates (methanol, ethanol, acetaldehyde); these products are formed by a different path.

Keywords
alkenyl · Fischer–Tropsch synthesis · labelling studies · rhodium compounds · vinyl

Introduction

Although the economic imperatives which led to the search for synthetic liquid fuels from catalytic conversions of syngas (Fischer–Tropsch reactions[1]) are largely no longer relevant, there is still considerable interest in the hydrogenation of carbon monoxide. This is partly because of the challenge of understanding a process in heterogeneous chemistry which appears to have no *direct* parallel in homogeneous reactions, and partly because of the expectation that a deeper understanding of the factors which control this and similar reactions will lead to new processes offering high-selectivity routes to useful compounds.

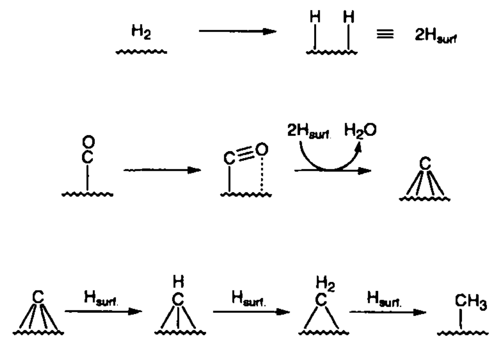
Fischer–Tropsch reactions are typically carried out by passing carbon monoxide and hydrogen over a heated catalyst (a metal on an oxide support); a complex mixture is often obtained, including alkenes, alkanes, alcohols, aldehydes and ketones. The main products are normally alkenes and alkanes and careful analysis shows that alk-1-enes are the primary products, which are later converted into alkanes. The overall reaction to give alkanes can be summarised by Equation (a).

$$n\mathrm{CO} + (2n+1)\mathrm{H}_2 \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O} \qquad \text{(a)}$$

The thermodynamics are favourable, with $\Delta H = 146$–$176\ \mathrm{kJ\,mol^{-1}}$, the exact value depending on n.

Early speculations by Fischer and Tropsch were that the reaction proceeded by hydrogenation of surface-adsorbed CO to surface methylenes, which then polymerised on the surface. Although a number of writers have disputed this,[2] it is now generally accepted that the formation of hydrocarbons (alkenes and alkanes) proceeds via surface methylenes. The early concepts were developed and extended, largely by Pettit[3] and Biloen[4] and their co-workers.

The major features of the stepwise process for the formation of methylene from CO adsorbed on a metal surface are represented by Scheme 1. Surface adsorbed CO dissociates on the



Scheme 1. The stepwise process for the formation of methylene from CO adsorbed on a metal surface (after Brady, Pettit, Biloen and Sachtler; ref. [3,4]).

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metal catalyst, in part aided by the oxide, to give surface carbide and surface-bound oxygen, which forms water with hydrogen. The carbide is then hydrogenated to form first methyne and then methylene. Hydrogenation occurs via surface hydrides formed by chemisorption of H_2.

Spectroscopic confirmation of the existence of surface species such as CH_2 was obtained from a study of nickel surfaces during a methanation reaction, where CO is hydrogenated to methane [Eq. (b)].[5] Although differing from a Fischer–Tropsch reaction in at least one essential, it is likely that the first steps on the surface will be similar.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \tag{b}$$

While there is general agreement concerning the involvement of methylene, there has been little consensus about the manner in which the polymerisations are initiated, propagated and terminated. A popular view is that elaborated by Brady and Pettit[3] in which a polymerisation of surface methylenes is initiated by a surface hydride or methyl. The chain carriers are therefore surface alkyls and the termination is a β-elimination giving the alkene. There are several problems with this view: it does not account for some formation of branched-chain hydrocarbons or for the formation of lower than expected amounts of C_2 species; even the β-hydride elimination, on a metal surface covered with hydrogen, is rather surprising. We and others, notably Knox and his collaborators,[6] have therefore explored the reactions of well-defined metal complexes as model systems, since this offered the possibility of investigating the methylene polymerisation under more controlled conditions.

Our work has involved the methyl-di(μ-methylene)-bis-(pentamethylcyclopentadienyl)dirhodium complexes, which efficiently decompose to give propene.[7] These complexes consist of an array composed of two μ-methylenes spanning two rhodiums, which also bear one (or two) methyls, and offer a miniature molecular model of a portion of a rhodium surface during a Fischer–Tropsch polymerisation reaction. Analysis of the decomposition of specifically labelled (^{13}C and ^2H) complexes showed that only the carbons and hydrogens of the C_1 ligands played a role in the C-C-C coupling reactions to give propene and allowed a mechanism to be described for this reaction.[8]

Surprisingly the results indicated the existence of a pathway to propene that is of lower energy than the straightforward coupling, that is, $CH_3 + CH_2 + CH_2$ or $H + CH_2 + CH_2 + CH_2$ followed by a β-elimination. The new, low-energy path implicated vinyl as a key intermediate species. We also found facile coupling of vinyl and μ-methylene in the complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(CH{=}CHR)_2]$ (R = H, (*Z*)-Me);[9] other authors have noted that couplings involving alkyls and vinyls or acyls proceed more easily than alkyl + alkyl coupling.[10]

This discovery then raised the question of whether the same pathway could exist in the real surface system, and hence whether vinylic species were also implicated in the heterogeneous Fischer–Tropsch reaction that the molecular complexes were modelling. In fact, the participation of some (but not precisely defined) C_2 species in Fischer–Tropsch reactions has been put forward by several authors.[11]

We have therefore investigated this possibility by adding vinylic probes to Fischer–Tropsch reactions over rhodium catalysts. Rhodium was chosen so as to allow a close match with our model systems, and since it shows interesting Fischer–Tropsch behaviour, in that oxygenates as well as hydrocarbons are formed.[12]

Quite a number of probe molecules (including ethene, cyclohexene, methanol, ethanol, nitromethane and nitroethane) have been used to investigate various aspects of Fischer–Tropsch reactions.[11, 13] We elected to use doubly ^{13}C-labelled vinyls—$^{13}CH_2{=}^{13}CHBr$, $(^{13}CH_2{=}^{13}CH)_4Si$ and $^{13}CH_2{=}^{13}CH_2$—as probes, since they were expected to give the most unambiguous mechanistic information. Analysis of the mass spectra of the organic products would immediately show 1) whether the $^{13}C_2$ probe had been incorporated into the products, and to what degree, 2) whether C–C cleavage of the probe to C_1 was significant and whether any C_n hydrocarbons were formed by such paths, 3) whether the C_2 probe initiated or propagated methylene oligomerisation, or both, and 4) what other reactions the probe molecule underwent.

Much attention has focused on the spectroscopic study of surfaces, in particular of metal single crystals;[14] unfortunately, however, the identification of a surface species does not necessarily infer that it contributes to the catalytic cycle. One example of this is ethylidyne ($CH_3C{\equiv}$), which has been often detected on surfaces, but which appears to be a "spectator species"[15] rather than an intermediate, for example, in hydrogenation of ethylene to ethane. Very recently new techniques have allowed reactions to be followed on single crystal surfaces under ultrahigh vacuum conditions; some of these are directly relevant to the studies reported in this paper (see below), and it is hoped that such measurements will eventually link up with our kinetic studies. Parts of the work have been published.[16, 17]

Experimental Procedure

Equipment: Quantitative analysis of the reaction products was carried out by gas chromatography on a Supelco SPB-1 (60 m × 0.53 mm × 5 µm) column. The level of ^{13}C incorporation was analysed by GC-MS (HP 3700–5171 A); the products were separated by a Chromosorb CPSil-5CB (50 m × 0.34 mm × 5 µm) or a Poraplot Q (30 m × 0.34 mm) capillary column, and the fractions of the isomers $^{13}C_x{}^{12}C_{n-x}$ of various molecular weight calculated by comparison with the unlabelled molecular-ion envelope.

Preparation of the Rh/Ce/SiO$_2$ catalyst: The catalyst was prepared by impregnation of the support (Davisil grade 645 silica gel) to incipient wetness in a two-stage process to give loadings of 9% CeO_2 and 4% Rh, respectively. In the first step, an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) was added, and the catalyst heated slowly to 373 K to drive off the water; this was followed by more rapid heating to 473 K. In the second impregnation step, addition of $Rh(NO_3)_3$ (14.07%, as a solution in nitric acid (17 M), Johnson Matthey) was followed by slow heating to 373 K, at which temperature the catalyst was fully dried. The catalyst (1 g in a fixed-bed microreactor, dimensions 6 × 350 mm) was reduced under a steady stream of hydrogen (1 atm, 500 $cm^3 h^{-1}$), with programmed heating (4 $K min^{-1}$) from room temperature to 673 K and 4 h at 673 K to ensure complete reduction. The catalyst was then cooled to the reaction temperature (473 K) under hydrogen and the gas flow switched to syngas (1 atm, $CO{:}H_2 = 1{:}2$; flow rate 500 $cm^3 h^{-1}$). Good reproducibility, with optimum activity and selectivity, was achieved after 10 h on stream. The full activation of the catalyst was performed initially and then at weekly intervals. However since the Rh/Ce/SiO_2 catalyst activity decreased with time on stream, a "partial" activation (a temperature-programmed reduction to 673 K at 4 $K min^{-1}$ under hydrogen), to burn off surface carbon that had accumulated on the catalyst, was carried out every 5 h. When vinyl bromide or tetravinylsilane were used as probes a further slow deactivation of the catalyst occurred. The products of the reaction were either sampled directly from the gas stream and analysed by gas chromatography or collected in a liquid-nitrogen trap and analysed by GC-MS. The latter method was used to collect enough of the higher molecular weight products for detection and GC-MS analysis. Quantification was achieved by calibration of the GCFID detector with standards of known molarity. For the runs with probes the products were analysed by both GC and GC-MS before, during and after probe additions. A background GC was initially obtained to show the distribution of products and activity. After a period of 1.5 h, the probe molecule (for example, $^{12}C_2H_4$ (BOC) as 6 × 280 µL pulses at 5 min intervals) was injected into the feed gas stream through a septum. A GC analysis was performed after the last injection. After a further 1.5 h period a final GC was carried out to ensure that the catalyst had returned to its initial unperturbed state. In each case a 250 µL sample was collected for analysis in a gas syringe over 5 s at a predetermined time after injection of the final pulse. Products were identified by comparison of their mass spectra with Wiley library spectra, stored in the HP ChemStation software. In some cases (e.g., methanol and acetaldehyde, hexane and hex-3-ene) it was not always possible to obtain good baseline separation of the peaks.

Labelled probe molecules: Doubly labelled ethene ($^{13}C_2H_4$; 99% ^{13}C) and vinyl bromide ($^{13}C_2H_3Br$; 99% ^{13}C) were obtained from MSD of Canada. Labelled tetravinylsilane was obtained by a modified literature procedure [18]. Labelled vinyl Grignard was prepared by treating vinyl bromide (99% $^{13}C_2H_3Br$; 1 g) with magnesium (0.22 g) in dry tetrahydrofuran (THF) under nitrogen; the reaction was initiated with a trace of 1,2-dibromoethane. The vinyl Grignard was then treated with $SiCl_4$ (0.24 g) in pentane (3.4 cm^3) and gently refluxed. Workup gave a solution of labelled tetravinylsilane in THF. Pure, labelled $Si(^{13}C_2H_3)_4$ was obtained by preparative GC, and analysis by GC-MS showed it to be ca. 99% labelled. Addition of the labelled probe molecule was accomplished by adding small quantities to the gas stream (ca. 52-fold molar excess of CO). Two methods of addition were used: 1) pulses of the probe (each 1.14×10^{-5} moles) were added at 5 min intervals to the synthesis gas (corresponding to 7.1×10^{-3} moles of carbon per hour), of which ca. 10% was converted, giving an effective ratio of probe to converted CO of ca. 1:5, or 2) a continuous dose of the probe was added. ^{13}C incorporation into each product was then found by comparison of mass spectra taken before and during addition for each product. A computer program was used to calculate the extent of ^{13}C labelling incorporated into each product. The results showed that the method of addition had very little effect on the extent of incorporation of the labelled probe or on the overall product distribution.

Results

Background data: Carbon monoxide was hydrogenated to hydrocarbons and oxygenates over a $Rh/Ce/SiO_2$ catalyst, in a flow microreactor operating under conditions of low conversion. The optimum operating regime used a stoicheiometric mixture of synthesis gas ($CO:H_2 = 1:2$; 1 atm; flow rate ca. 500 cm^{3}h^{-1}) over 1 g of catalyst held at 498 K (Fig. 1). The total product activity was ca. 700 µmol(C equiv)gcat^{-1}h^{-1}, and CO conversion was less than 10%; the amount of CO_2 formed was very small and was neglected.

A plot of log(W/N) against N (W = weight fraction, N = number of carbon atoms in that fraction) gave a typical Anderson–Schulz–Flory distribution for a Fischer–Tropsch reaction (Fig. 1) with high C_1 and low C_2 fractions and a monotonic decrease from N = 3–7, indicative of a step growth polymerisation. The majority of the hydrocarbons were linear alkenes, but some linear alkanes and some branched alkenes together with some oxygenates (ethanol, a little acetaldehyde, traces of methanol and propanol) were produced. The measured chain-growth probabilities (α) for the C_3 to C_7 fractions gave good straight line plots. A typical value for α was found to be 0.52 from the gradient and 0.53 from the intercept.

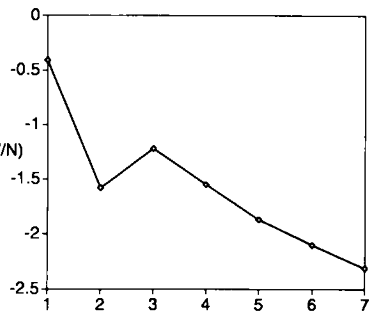


Fig. 1. Anderson–Schulz–Flory plot of the formation of hydrocarbon products from CO hydrogenation after 1.5 h on stream. Plot of log(W/N) against N, where W is the weight fraction of products having carbon number N.

The effect of adding a probe: The effect of adding the probes was to increase the formation rate of each straight-chain hydrocarbon product (Fig. 2).[19] Three sets of data are given for each probe: The first set give the initial measurements, when the catalyst has reached equilibrium, after approximately 1.5 h on stream. The third set were measured 1.5 h after the probe had been added and confirm that the system returned to equilibrium after addition. The second set of histograms show the effect of the probe molecule by plotting the change in hydrocarbon production during its addition. The chain-growth probabilities (α) calculated from these data sets are collected in Table 1.

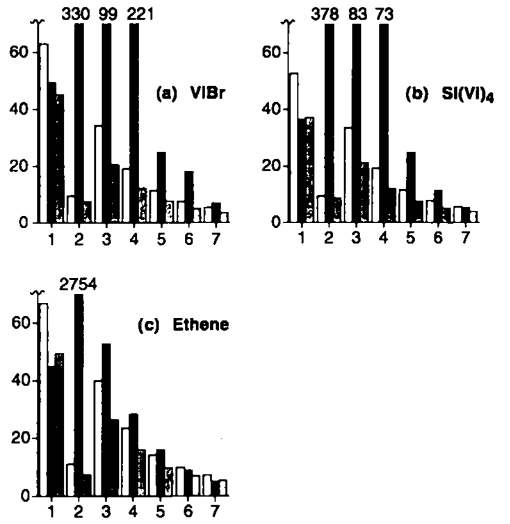


Fig. 2. Plot of product formation rate (y axis, nmol(carbon)gcat^{-1}s^{-1}) against carbon number (x axis) before (□), during (■) and after (▮) addition of probe.

Table 1. Effect of probe addition on probability of chain growth α [a].

	α [b]	α' [c]	α [d]
vinyl bromide	0.51	0.41	0.52
tetravinylsilane	0.52	0.40	0.53
ethene	0.53	0.45	0.55
ethyl bromide	0.52	0.55	0.56
tetraethylsilane	0.55	0.56	0.56

[a] α is calculated from the gradient of a graph of log(W/N) against N, where W is the weight fraction of products with carbon number N. Products in the range C_3 to C_7 were analysed. [b] α before probe addition. [c] α' during probe addition. [d] α after probe addition.

Table 2a. Incorporation of $^{13}C_x$ from the $^{13}C_2H_3Br$ probe (6 × 280 µL) [a].

x	0	1 [b]	2	3	4	5	6	7
methane	98	2(1)						
ethane	30	0(1)	70	0				
ethene	92	2(2)	6					
propene	63	3(2)	31	3				
butane	38	1(2)	10	2	49			
but-1-ene	51	4(2)	7	3	35			
trans-but-2-ene	35	3(2)	9	3	50			
cis-but-2-ene	37	3(2)	8	3	48			
pentane	75	4(4)	14	1	4	1		
pent-1-ene	85	4(5)	6	1	3	1		
trans-pent-2-ene	76	4(4)	11	1	6	1		
cis-pent-2-ene	81	4(4)	10	1	4	1		
hex-1-ene	81	5(5)	5	1	4	1	4	
trans-hex-2-ene	86	5(6)	6	1	1	0	2	
cis-hex-2-ene	86	5(6)	5	1	1	0	2	
heptane	89	6(7)	4	1	0	0	0	0
hept-1-ene	84	8(6)	4	1	2	0	1	0
trans-hept-2-ene	91	6(7)	3	0	0	0	0	0
cis-hept-2-ene	90	6(7)	3	0	0	0	0	0
hept-3-ene	87	7(7)	4	1	1	0	0	0
acetaldehyde	97	2(2)	0					
ethanol	97	2(2)	0					

[a] Amount of probe injected; see text. [b] Figures in parentheses are the expected % $^{13}C_1$ at natural abundance.

The incorporation of $^{13}C_x$ ($x = 0, 1, 2, \ldots n$) into a C_n hydrocarbon from a $^{13}C_2$-labelled probe (99%) is summarised in Tables 2a–c. The results are given as the absolute percentages of $^{13}C_x$ detected in the products during addition of vinyl bromide,

Table 2b. Incorporation of $^{13}C_x$ from $Si(^{13}C_2H_3)_4$ (6 × 1.0 μL) [a].

x	0	1 [b]	2	3	4	5	6	7
propane	73	4(2)	23	0				
propene	82	3(3)	14	1				
cyclopropane	0	5(0)	92	3				
butane	67	4(3)	7	2	20			
but-1-ene	76	4(3)	4	2	14			
trans-but-2-ene	64	3(3)	6	2	25			
cis-but-2-ene	65	4(3)	6	2	24			
pentane	61	4(4)	5	2	28	1		
pent-1-ene	69	5(4)	3	1	22	0		
trans-pent-2-ene	55	3(3)	4	1	37	1		
cis-pent-2-ene	57	3(3)	4	1	34	1		
hex-1-ene	86	7(6)	1	0	5	0	0	
trans-hex-2-ene	85	6(6)	4	0	3	0	2	
cis-hex-2-ene	81	8(5)	5	0	4	0	2	
heptane	87	8(7)	4	0	0	0	0	0
hept-1-ene	87	8(7)	0	0	0	0	0	0
trans-hept-2-ene	89	8(7)	3	0	0	0	0	0
cis-hept-2-ene	90	8(7)	2	0	1	0	0	0
hept-3-ene	87	8(7)	5	0	1	0	0	0
acetaldehyde	96	3(2)	1					
ethanol	93	7(2)	0					

[a] Amount of probe injected; see text. [b] Figures in parentheses are the expected % $^{13}C_1$ at natural abundance.

Table 2c. Incorporation of $^{13}C_x$ from $^{13}C_2H_4$ (6 × 280 μL) [a].

x	0	1 [b]	2	3	4	5	6	7
methane	99	2(1)						
ethane	31	0(0)	69					
ethene	15	0(0)	85					
propane	86	4(3)	10	0				
propene	86	7(3)	6	1				
butane	87	6(4)	6	0	2			
but-1-ene	92	4(4)	3	0	1			
trans-but-2-ene	86	4(4)	5	1	4			
cis-but-2-ene	87	4(4)	5	1	4			
pentane	86	9(5)	4	0	1	0		
pent-1-ene	92	6(5)	2	0	0	0		
trans-pent-2-ene	89	5(5)	5	0	0	0		
cis-pent-2-ene	89	5(5)	5	0	0	0		
hex-1-ene	94	3(6)	0	0	2	0	1	
trans-hex-2-ene	88	8(6)	2	1	1	0	0	
cis-hex-2-ene	90	8(6)	2	0	0	0	0	
heptane	90	9(7)	1	0	0	0	0	0
trans-hept-2-ene	93	7(7)	0	0	0	0	0	0
cis-hept-2-ene	87	9(7)	0	0	0	0	1	2
hept-3-ene	93	7(7)	0	0	0	0	0	0
acetaldehyde	96	4(2)	0					
ethanol	97	2(2)	0					
propanol	85	5(3)	9	0				

[a] Amount of probe injected; see text. [b] Figures in parentheses are the expected % $^{13}C_1$ at natural abundance.

tetravinylsilane or ethene, respectively. The expected natural abundance percentages of $^{13}C_1$ are also given in parentheses. No data for C_1 or C_2 products were obtained for the tetravinylsilane reactions; methanol and acetaldehyde, hexane and hex-3-ene, and occasionally hept-1-ene were difficult to obtain with good enough baseline separation for useful analysis. In addition, cyclopropane was only seen in the tetravinylsilane, and propanol in the ethene experiments.

In addition to the probe molecules, which were incorporated in the Fischer–Tropsch reaction, a number of others, including bromoethane and tetraethylsilane (Fig. 3), were investigated. Addition of bromoethane resulted in a sharp increase in ethane formation; this indicates that there had been some cleavage of the C–Br bond, but there was no significant increase in the rate of formation of any of the higher hydrocarbons. When tetraethylsilane was injected as a probe, there was no effect at all, even on the rate of production of C_2 hydrocarbons; the molecule was quite inert and passed unchanged straight through the catalyst. We conclude that such ethyl probes are not incorporated.

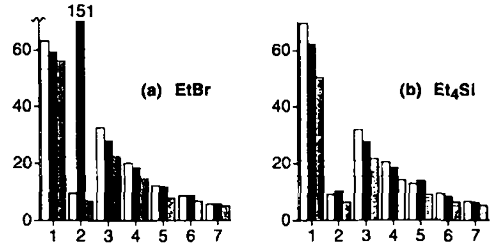


Fig. 3. Plot of product formation rate (*y* axis, nmol(carbon)gcat^{-1}s^{-1}) against carbon number (*x* axis) before (□), during (■) and after (▮) addition of probe.

Discussion

Background data: The use of the rhodium/ceria/silica catalysts for carbon monoxide hydrogenation gave a typical distribution of Fischer–Tropsch hydrocarbon products. The amounts produced followed a modified Anderson–Schulz–Florey plot, and showed a dip at C_2, in agreement with results reported by other workers.[2] Qualitative observations showed that the effect of adding the ceria on hydrocarbon formation was to increase the activity of the rhodium, as had already been reported.[12]

Addition of unlabelled probe molecules: In each case the effect of adding the probe molecules vinyl bromide, tetravinylsilane or ethene (Fig. 2) was to increase the amount of $C_{\geq 2}$ hydrocarbons produced. The effect was largest, as might be expected, for the formation of ethane (and some ethene) by hydrogenation/hydrogenolysis. In no case was there any appreciable change in the amount of methane formed.

Separate experiments also showed that other C_2 probe molecules, in particular tetraethylsilane and bromoethane, did not participate in the growth process. Tetraethylsilane passed through the catalyst (Fig. 3b) without any apparent interaction, and while bromoethane was hydrogenolysed to some extent, there was no indication of any incorporation of C_2 in the higher Fischer–Tropsch products (Fig. 3a). The effect of adding a probe molecule, when it was incorporated, was to lower α (the chain-growth probability) from 0.51–0.53 to 0.40–0.45 (Table 1); when the probe molecule was not incorporated, there was no change in α. Thus we can say that although the C–Br bond of bromoethane is broken on the catalyst, the ethyl species, which is presumably formed, does not initiate methylene oligomerisation. It appears that the organic residue must be unsaturated for incorporation to take place.

It should be noted that recent studies on clean single crystal metal surfaces under ultra-high vacuum conditions have now offered substantial confirmation that carbon–halogen bonds are easily cleaved on a wide variety of transition metals to give surface metal alkyls, and that the activation energy is quite modest, for example, only around 20 kJ mol^{-1} for a C–I bond.[20] Although less has been reported concerning unsaturated halides, the formation of vinyl on a Pt(111) surface from vinyl iodide[21] and of phenyl on Cu(111) from iodobenzene[22] have both been described. Thus there is ample evidence for the concept that σ-bonded organometallics (or related surface alkyls) result from the reaction of organic halides with transition metal surfaces.

Our results on the lack of reaction of bromoethane (as opposed to vinyl bromide) as a probe under syngas catalytic conditions on rhodium may be contrasted with those of Bent and co-workers who reported the formation of propene from iodoethane and diiodomethane (presumably giving C_2H_5 and CH_2) on a Cu(100) surface under ultra-high vacuum conditions.[23] Such ultra-clean surfaces may show an idealised chemistry.

Addition of $^{13}C_2$-labelled probe molecules *$^{13}C_1$-incorporation data*: The incorporation data in Tables 2a–c show that the amount of $^{13}C_1$ detected matches the expected natural-abundance percentages quite closely and the two numbers are generally within $\pm 1\%$ of each other. This shows that there has been practically *no incorporation of* C_1 into the hydrocarbon products. This is confirmed by the methane figures, which show $^{13}C_1$ at natural-abundance levels for the vinyl bromide and ethene probes. For the ethene probe, even when the concentration of $^{13}C_2H_4$ was doubled, there was still no $^{13}C_1$ label in methane. Thus we can immediately conclude that C–C splitting (hydrogenolysis) of the vinylic probes does not occur under these conditions.

$^{13}C_2$-incorporation data: Addition to the CO/H_2 stream of any of the $^{13}C_2$-vinylic probes gave clear indications of the incorporation of $^{13}C_2$ into the hydrocarbon products. In all three cases this is highly significant, as the percentage of $^{13}C_2$ in a molecule at natural abundance should be very small: even for the largest molecules studied here, C_7, it is expected to be only 0.2%, well below the limits of detection, while the natural abundance of $^{13}C_2$ expected for smaller molecules is still less. Of the three probe molecules investigated, vinyl bromide ($^{13}C_2H_3Br$) was the most convenient for study as it led to the highest degree of incorporation.

The levels of $^{13}C_2$ incorporation found in the Fischer–Tropsch products is shown in the third column of Tables 2a–c. The incorporation of $^{13}C_2$ is largest into the C_3 fraction (propene and propane), and remains significant in the alkenes and alkanes up to C_7; it is also clear that the level of incorporation decreases with increasing size of the hydrocarbon. This phenomenon is expected from our mechanistic analysis (see below).

The results can be summarised: 1) the hydrocarbons show significant incorporation of $^{13}C_2$, but there is essentially no $^{13}C_2$ incorporation into the oxygenates, 2) the degree of incorporation found from the three probes decreases in the order vinyl bromide > tetravinylsilane > ethylene, and 3) the amount incorporated decreases with increasing molecular weight of the hydrocarbon.

$^{13}C_2$ incorporation appears to be slightly higher in the alkanes and may be slightly lower in the alk-1-enes, but the differences are small and therefore, at the level of accuracy where we have confidence, we propose that similar degrees of incorporation of $^{13}C_2$ occur into all the hydrocarbons of a given C_n. To a first approximation, the data are consistent with a similar origin for all the hydrocarbons of a given C_n. As operation at lower temperatures generally gives more α-olefins, it may be presumed that these are the initial reaction products and that the internal olefins and the alkanes are formed from them by isomerisation/hydrogenation over the catalyst.

When tetravinylsilane was used as probe some cyclopropane was formed; the use of $Si(^{13}C_2H_3)_4$ as probe together with ^{12}CO gave mainly $^{13}C_2$ cyclopropane. As has been discussed before,[24] a plausible route for cyclopropane formation involves the cyclopropanation of vinylsilane by a surface (i.e., rhodium-bound) methylene, followed by cleavage of the C–Si bond by a surface hydride to release the cyclopropane. This path is an alternative to the reaction of surface methylene with surface vinyl, which leads to linear homologation to give higher alkenes. In contrast to tetravinylsilane, vinyl bromide is much more effective in linear homologation and quite inactive for cyclopropanation; this is also consistent with our data that the transfer of vinyl to rhodium from tetravinylsilane occurs with greater difficulty than from vinyl bromide.

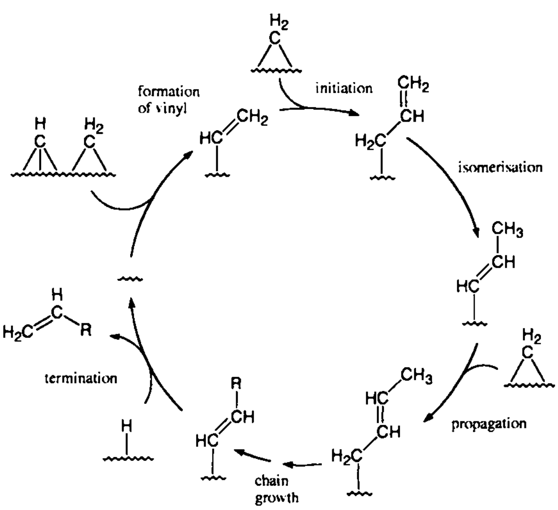
$^{13}C_3$-incorporation data: $^{13}C_3$ incorporation was also very low, close to that expected for natural abundance for the most part. However, there appeared to be some $^{13}C_3$ incorporation in the C_3 and C_4 hydrocarbons when vinyl bromide or ethene were used as probes. The origin is not clear: it may arise from some fragmentation of the $^{13}C_4$ and the $^{13}C_4{}^{12}C$ hydrocarbons, which are formed in substantial degree (see below).

$^{13}C_4$-incorporation data: Apart from the incorporation of $^{13}C_2$ into the hydrocarbons, the other dramatic result is the significant incorporation of $^{13}C_4$ into the C_4, C_5 and C_6 hydrocarbons. This is especially clear when vinyl bromide was used as probe, but is even evident in the experiments using ethene, the least incorporated probe. It can only arise from a coupling of two fragments containing $^{13}C_2$. We have recently shown that σ-vinyls on rhodium and iridium η^5-pentamethylcyclopentadienyl complexes do couple to C_4 very easily;[25] further, the stoicheiometric coupling of vinyls on single metal crystal faces to give butadiene has also been reported,[26] and this may be a model for the formation of the $^{13}C_4$ hydrocarbons in our experiments. Presumably the first product is also butadiene here, which is then hydrogenated to butenes and butane. The origin of the $^{13}C_4{}^{12}C$ labelling of the C_5 fraction is not so clear. Since the largest amount was seen in the reactions where tetravinylsilane is used as probe, one possible explanation is that it arises from an intramolecular coupling in a cyclopropyl(vinyl)silane, $SiR_2(^{13}CH{=}^{13}CH_2)(^{13}CH^{13}CH_2{}^{12}CH_2)$, which might be intermediate in the formation of cyclopropane (see above).

Labelling of oxygenates: There was no incorporation of ^{13}C above natural abundance into the oxygenates (methanol, ethanol or acetaldehyde) or into CO_2; this shows that they are not formed from vinyl groups. The only exception is *n*-propanol, which arises in the experiments with $^{13}C_2H_4$ as the probe; here a significant level of $^{13}C_2$-propanol is formed. The $^{13}C_2$-labelling can be attributed to a rhodium-promoted hydroformylation of ethene, rather than a Fischer–Tropsch reaction, and these data show that the C_1 and C_2 oxygenates must arise by completely different pathways from those used to build up the hydrocarbons. This has been discussed by other workers and model schemes have been proposed.[12]

Alkenyl model for Fischer–Tropsch polymerisation of surface methylenes: The data in Tables 2a–c show that there is most incorporation of $^{13}C_2$ (and of $^{13}C_4$) and very little, if any, of $^{13}C_1$, $^{13}C_3$, etc. Thus the probe molecules are not significantly cleaved under our conditions, nor is any other mechanism operating that incorporates odd numbers of ^{13}C atoms. The data also show that the degree of $^{13}C_2$ incorporation decreases with increasing number of carbons in the hydrocarbon product. This is consistent with the C_2 species being involved in chain initiation rather than chain propagation.

In order to understand the $^{13}C_2$-incorporation data further, we have developed a new alkenyl model for Fischer–Tropsch polymerisation of surface methylenes. The absorption, activation and cleavage of CO on a metal to give a surface carbide species have all been well established, as has the hydrogenation of this last species to surface methyne and methylene (Scheme 1). As discussed above, we need to diverge from previous hypotheses involving alkyl chain propagation, since we now have to accommodate the new data showing the incorporation of C_2 (vinyl). It is particularly significant, we believe, that vinyl, especially derived from vinyl bromide, is such an excellent initiator, while ethyl, as ethyl bromide, is ineffective. We therefore propose that the participation of vinyl is an integral part of the surface polymerisation mechanism. This is shown in the form of a conventional catalytic cycle in Scheme 2, where the first step (top left) is the formation of a surface vinyl. Each succeeding step consists of the (irreversible) linear homologation of a surface alkenyl species with surface methylene, followed by an isomerisation of the resulting allylic species to another alkenyl. Growth can be terminated by reaction with surface hydrogen or in other ways (see below). For simplicity the diagram is restricted to the linear propagation; however, it can readily be shown that the allylic intermediates such as -$CH_2CH{=}CHR$ can also isomerise to -$C(CH_3){=}CHR$ and that reaction with surface CH_2 is then possible at the alkenyl C. This will be inhibited on steric grounds; this explains both the formation of branched-chain isomers and also their low abundance.[19]

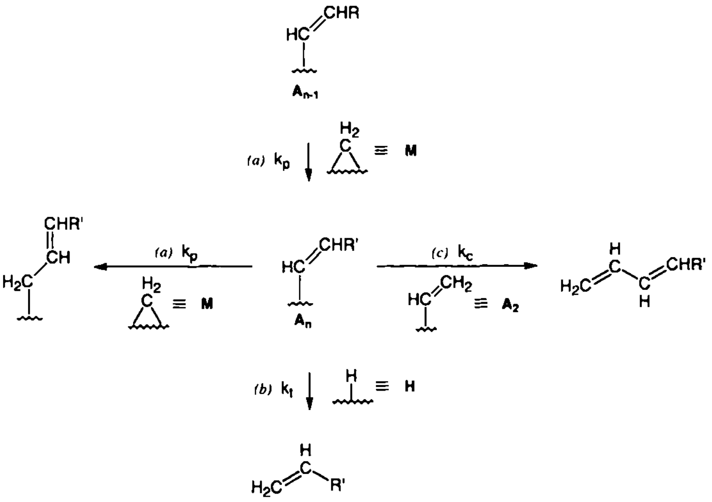


Scheme 2. Representation of the catalytic cycle for the formation of alk-1-enes, based upon methylene plus alkenyl coupling on the metal surface.

We suggest that, in the absence of a vinylic probe, the initial formation of a surface vinyl (-$CH{=}CH_2$) occurs by the reaction of a surface methyne ($\equiv$CH) and a surface methylene ($=CH_2$). Although this reaction does not yet seem to have been demonstrated on a surface, it has been modelled in organometallic complexes, for example, the interaction of a tungsten carbyne with a diruthenium μ-methylene gives a trimetallic cluster bonded to an alkenyl [Eq. (c)].[27]

$$[\{C_5H_5Ru\}_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(MeCN)] + [\{C_5H_5W\}(CO)_2(\equiv CR)] \longrightarrow [(RCH{=}CH)\{C_5H_5W\}(CO)_2\{C_5H_5Ru(CO)\}_2] \quad (c)$$

In order to quantify the data for the polymerisation mechanism, we need to consider not only the propagation steps (Scheme 3, a), but also chain termination by hydrogen transfer (b) and by coupling (c).



Scheme 3. The processes involved in the surface reactions: a) propagation by coupling of alkenyl with methylene, b) termination by reaction of alkenyl with hydrogen and c) termination by coupling of alkenyl with vinyl ($R' = CH_2R$).

If the rate constants (k_p) for each step of the linear propagation of each surface alkenyl species (-$CH{=}CH\text{-}R = A_n$) with methylene ($=CH_2 = M$) are similar, then the rate of appearance of a species A_n will be given by the rate of reaction to form it, $k_p[A_{n-1}][M]$. Under steady state conditions, the rate of formation must equal the rate of disappearance by a) propagation ($k_p[A_n][M]$) plus b) chain termination by hydrogen transfer ($k_t[A_n][H]$). Hence, Equation (1) can be derived.

$$d[A_n]/dt = k_p[A_{n-1}][M] - k_p[A_n][M] - k_t[A_n][H] = 0 \quad (1)$$

Equation (1) can be re-written as Equation (2) to give $[A_n]/[A_{n-1}]$, which equals α, the chain growth probability.

$$[A_n]/[A_{n-1}] = k_p[M]/\{k_p[M] + k_t[H]\} = \alpha \quad (2)$$

During addition of a vinyl probe a second termination step, coupling with an A_2 species (Scheme 3, c), becomes significant (see Tables 2a–c, and discussion below). We suggest that this process is negligible in the absence of added initiator probe. Hence the rate of coupling with an A_2 species can be expressed by $k_c[A_n][A_2]$, leading to Equation (3),

$$d[A_n]/dt = k_p[A_{n-1}][M] - k_p[A_n][M] - k_t[A_n][H] - k_c[A_n][A_2] = 0$$

from which $[A_n]/[A_{n-1}]$ is given by Equation (4),

$$[A_n]/[A_{n-1}] = k_p[M]/\{k_p[M] + k_t[H] + k_c[A_2]\} = \alpha' \quad (4)$$

where α' is the modified chain growth probability. This extra termination step (c) explains why the chain-growth probability decreases on addition of a vinylic probe (Table 1). One can calculate the expected level of $^{13}C_2$ incorporation for different assumed fractions of labelled A_2 in the surface using Equation (2). For $\alpha = 0.52$, even with 100% $^{13}C_2$ in A_2, the label is detectable only up to C_9 hydrocarbons. The equation also allows the amount of $^{13}C_2$ present in the surface vinyls, A_2, to be estimated from a knowledge of the labelling found in the C_3 and higher hydrocarbons. This is shown in Figure 4, which plots the percentage of a given product expected to be $^{13}C_2$-labelled for a given $^{13}C_2$-vinyl concentration at the surface (dotted lines), and compares it to the experimentally determined $^{13}C_2$ incorporation (solid lines).

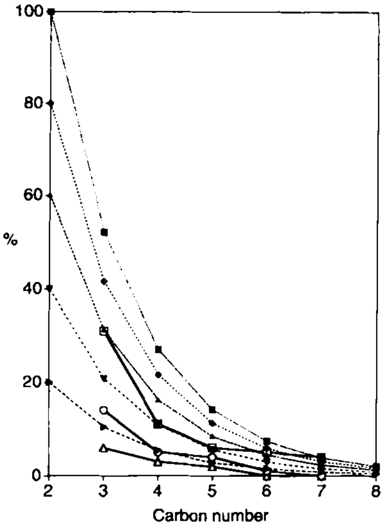


Fig. 4. Comparison between calculated $^{13}C_2$ incorporation assuming different initial surface concentrations of $^{13}C_2H_3$ (dotted lines: ···■··· 100%, ···◆··· 80%, ···▲··· 40%, ···▶··· 20%) and experimental $^{13}C_2$ incorporation derived from vinyl probes (bold lines: –□– $^{13}C_2H_3Br$, –○– $(^{13}C_2H_3)_4Si$; –△– $^{13}C_2H_4$): plot of percentage of coupled products that are $^{13}C_2$-labelled (y axis) against carbon number (x axis).

The calculation can be illustrated by the following example: If it is assumed that initially 20% of the surface vinyl is $^{13}C_2$-labelled (i.e., $[A_{n-1}] = 20\%$) and that $\alpha = 0.52$, then 52% of $^{13}C_2H_3$ will undergo propagation with methylene, and the amount that becomes incorporated into propenyl will be $0.52 \times 20\% = 10\%$. Therefore 10% of propene will be $^{13}C_2$-labelled. Similarly 52% of $^{13}C_2$-labelled propenyl will undergo homologation to form $^{13}C_2$-labelled but-1-enyl, and 5% of but-1-ene will be $^{13}C_2$-labelled (i.e., $0.52 \times 10\% = 5\%$), and so on. This calculation can be done for different assumptions of initial $^{13}C_2$ surface vinyl.

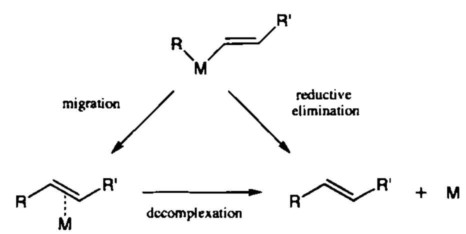
For $^{13}C_2H_3Br$ there is some 30% incorporation of $^{13}C_2$ into the C_3 and approximately 11% incorporation of $^{13}C_2$ into the C_4 hydrocarbons (neglecting vinyl-vinyl coupling). These values are consistent with a level of initiation of around 60% by added $^{13}C_2H_3$. Thus vinyl bromide is an extremely effective promoter of Fischer-Tropsch polymerisation.

Similar procedures were applied to the data with $Si(^{13}C_2H_3)_4$ or $^{13}C_2H_4$ as probes; however, here the degree of incorporation of the $^{13}C_2$ is significantly less. This suggests that these molecules are less effective precursors of surface vinyls with initiation of around 30% by added $^{13}C_2H_3$ from tetravinylsilane and 10% from ethene.

While a precise definition of this effect needs more work, it may arise from the differing sp^2 C–X bond strengths. The $CH_2{=}CH{-}X$ bond energy is only known for $X = H$ (444 kJ mol^{-1}), but one might expect that the relative ease with which the sp^2 C–X bonds are broken may be similar to that for sp^3 C–X bonds, that is, $X = Br > Si > H$.[28]

A useful internal check can be made: If 60% of the surface vinyl is labelled and incorporated into Fischer-Tropsch products, this means that adding the $^{13}C_2$ vinyl bromide causes an approximately 2.5-fold increase in surface vinyl [(60 + 40)/40]. This compares very closely to the increase in the rate of product formation measured on the addition of the vinyl bromide (2.9-fold). Similarly, when $^{13}C_2$ ethylene is added, approximately 10% of surface vinyls are labelled, and a 1.1-fold increase in surface vinyls [(10 + 90)/90] results; the rate of formation of products on addition of the ethylene increases by a factor of 1.3. This indicates that the model that forms the basis of the calculations is correct.

The reason why the alkenyl-intermediate mechanism is favoured over the alkyl-intermediate mechanisms, previously proposed, is because the intermediates (containing metal-bound alkenyl sp^2 carbons) can couple with metal-bound alkyl sp^3 carbons (i.e., methylenes) with a lower activation energy. Several workers have noted that the coupling of a metal-bound alkenyl sp^2 carbon to a metal-bound alkyl sp^3 carbon is generally preferred to the coupling between two metal-bound alkyl sp^3 carbons.[10] It is suggested that the former can occur as a *migration* process (followed by decomplexation) with a lower activation energy, while the latter is a direct reductive elimination. The two paths are illustrated schematically in Scheme 4. Calhorda et al. have provided theoretical explanations for such concepts in coupling reactions on palladium and nickel complexes in solution.[29]



Scheme 4. The two possible processes for coupling of an alkyl and an alkenyl on a metal: reductive elimination contrasted with migration followed by decomplexation.

Summary

Our ^{13}C-labelling data show clearly that a C_2 species is responsible for the initiation of the polymerisation of surface methylenes in the Fischer-Tropsch reaction. By implication, based on our model studies, and directly, from the failure of ethyl to act as an initiator, we suggest that the real initiator is a surface vinyl. We have put forward a cycle for the polymerisation involving the reactions of surface methylenes with surface alkenyls, and terminated by reactions of the alkenyls with surface hydrogen or by a vinyl-alkenyl coupling. There is good agreement between the predictions made and the data from $^{13}C_2$ labelling experiments. Since the new mechanism involves different types of reactions to form C_2 and $C_{>2}$ hydrocarbons, respectively, it is not expected that the amounts of C_2 products will lie on the normal polymerisation curve. This mechanism can account for the formation of lower than expected amounts of C_2 and of small amounts of branched-chain hydrocarbons, and does not require a β-hydride elimination step.

In addition to the polymerisation of methylenes mediated by surface alkenyl species, we have also discovered an additional process in which the added probe C_2 molecules are dimerised to C_4. This seems to be a facile process in the catalytic system and to occur very easily for vinyl to butadiene on clean metal crystal surfaces too.

Surface vinyls have recently been made and have been found to react in similar ways to that postulated here, for example, by coupling with surface alkyls and dimerisation to C_4.[21, 25] Although a vinyl initiator is the most likely, the participation of certain other C_2 species [for example, a surface vinylidene $CH_2{=}C{=}$] cannot definitively be ruled out. In view of the great lability of hydrogens on metal surfaces such species may also be involved, and there could indeed be an equilibrium between a vinylidene and a vinyl. This point will be investigated further shortly. However, we note that vinylidene species as intermediates in Fischer–Tropsch reactions were specifically considered by McCandlish[30] but were excluded, largely on the basis of experiments on model systems, by Hoel and his collaborators.[31]

Further, although our data clearly show the importance of vinylic initiators over rhodium catalysts we cannot at the moment rule out that "normal alkyl–alkyl" coupling between methylenes or between surface alkyls and methylenes can sometimes occur. We are currently investigating other conditions (e.g., higher temperatures) and other metal catalysts to see how general our conclusions will prove to be.

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