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Catalysis Today 71 (2002) 343–349

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Some evidence refuting the alkenyl mechanism for chain growth in iron-based Fischer–Tropsch synthesis

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Abstract

Recently, Maitlis et al. [J. Catal. 167 (1997) 172] proposed an alternative reaction pathway for chain growth in the Fischer–Tropsch synthesis. In this mechanism, chain growth is assumed to occur by methylene insertion into a metal–vinyl bond, forming an allyl species that will subsequently isomerise to a vinyl species. Organo-metallic allyl complexes, $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$ and $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$ were synthesised. Under thermal treatment, the decomposition of these complexes was observed, instead of the isomerisation. In a hydrogen atmosphere, the reduction of the iron–carbon bonds and the hydrogenation yielding iron–alkyl species was observed. This clearly shows that the proposed vinyl–allyl isomerisation is unlikely to occur in mono-nuclear iron complexes. Hence, it might be expected that the reaction mechanism proposed by Maitlis et al. [J. Catal. 167 (1997) 172] is unlikely to be the main route for chain growth in the Fischer–Tropsch synthesis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Iron; Alkenyl; Mechanism

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1. Introduction

The Fischer–Tropsch synthesis has been defined as the hydrogenation of carbon monoxide yielding higher molecular weight hydrocarbons on heterogeneous catalysts [1]. The specific characteristic of the Fischer–Tropsch synthesis is the inhibition of desorption of the surface species, so that chain growth can become the dominant reaction [2]. The mechanisms on the formation of higher hydrocarbons in the CO hydrogenation have been debated in literature since the first report on this reaction in 1923 [3]. The generally accepted reaction pathway (see Fig. 1) for the formation of higher hydrocarbons proceeds via the dissociation of carbon monoxide [4,5], surface carbon is then hydrogenated to CH_x surface species [6,7]. The participation of CH_x surface species in the chain growth process has been clearly demonstrated by van Barneveld and Ponec [8], and Brady and Pettit [9,10]. The formation of oxygenates may proceed via a CO insertion [11].

Maitlis et al. [12] proposed that polymer chain carriers are surface alkenyl species rather than alkyl species. This was based on their observation of propene, methane and traces of C_2 and C_4 hydrocarbons as the decomposition products of $[\{C_5(CH_3)_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ upon heating till 330 °C. Fig. 2 shows schematically the mechanism using a surface alkenyl species as the key intermediate [13]. In this mechanism, it is proposed

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PII: S0920-5861(01)00461-8

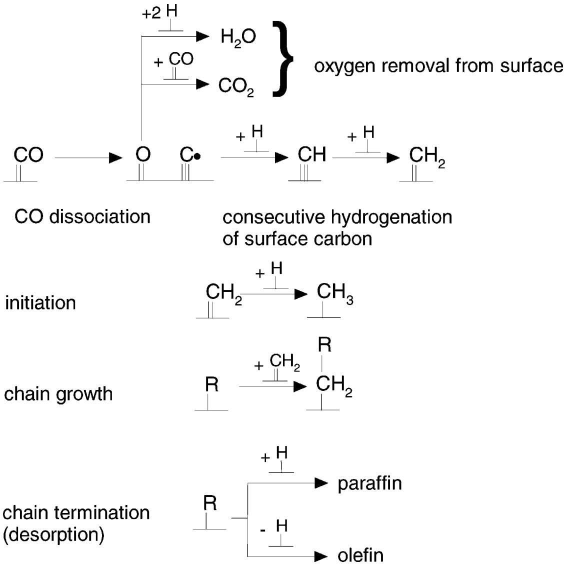

Fig. 1. Generally accepted reaction pathway for the formation of higher hydrocarbons in Fischer–Tropsch synthesis.

that dissociation of chemisorbed CO and subsequent hydrogenation of the surface carbon yields surface methyne (≡CH) and surface methylene (=CH_2) species. These surface species can then react further to form a surface vinyl species (–CH=CH_2), which is the chain starter. Chain growth can then take place via a step-wise polymerisation, where a surface methylene species reacts with the vinyl species to form an allyl species (–CH_2CH=CH_2). The allyl species can then isomerise to an alkenyl species. Termination can occur by the reaction between surface hydrogen and the surface alkenyl species yielding α-olefins.

The mechanism proposed by Maitlis et al. [13] cannot fully explain the mechanism of the Fischer–Tropsch synthesis. Primary selectivity for paraffins in the Fischer–Tropsch is typically in the range 20–30 mol% [15,16]. According to the mechanism proposed by Maitlis et al. [13], the primary selectivity for *n*-paraffins should be 0 mol%. This mechanism may, however, explain (partially) the formation of the α-olefins as a primary product in the Fischer–Tropsch synthesis.

The key step in the mechanism proposed by Maitlis et al. [13] is the allyl–vinyl isomerisation. Evidence for the possibility of such a facile isomerisation has been reported by Torkelson et al. [17], who observed the rearrangement of $[Ir_2(CH)_3(CO)_2(\mu\text{-}RC{=}CR)(dppm)_2]^+$ to $[Ir_2H(CH)(CO)_2(\mu\text{-}\eta^1, \eta^3\text{-}CH(R)C(H)R(dppm)_2]^+$ at room temperature. Based on this result, Maitlis et al. [18] proposed a mechanism for the allyl–vinyl isomerisation (see Fig. 3). It must, however, be stressed that the vinyl species was not obtained by Torkelson et al. [17]. They could only show the existence of $\eta^{1,3}$-vinylcarbene complex.

The critical step in the mechanism for chain growth as proposed by Maitlis et al. [13] is the allyl–vinyl isomerisation. In order to investigate the feasibility of this isomerisation step, metallo-organic model compounds were synthesised, which contain a Fischer–Tropsch active metal (iron) and as a ligand the species involved (see Fig. 4). To simulate a surface allyl species, allyl cyclopentadienyl dicarbonyl iron, $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$ **1**, and allyl cyclopentamethyl dicarbonyl iron **2**, $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$ were synthesised. To simulate a surface vinyl species, vinyl cyclopentadienyl dicarbonyl iron, $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH{=}CHCH_3\}$ **3**, was synthesised.

2. Experimental

The model compounds were synthesised and characterised using mass spectrometry (VG Micromass 16F), IR (Perkin Elmer 1000 FTIR) and ^{1}H-NMR (Varian XR-2000/Varian Unity 4000).

2.1. Synthesis of metallo-organic model compounds

*Synthesis of allyl cyclopentadienyl dicarbonyl iron, $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$,**1**.* $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$ **1** was synthesised using a modification of the procedure proposed by Green and Nagy [19]. A sodium amalgam solution was prepared by stirring 77.2 g mercury with 0.811 g sodium for 5 min. 1.54 g cyclopentadienyl dicarbonyl iron dimer, $(Fe\{[C_5H_5](CO)_2\})_2$ dissolved in 10 ml THF was added. The solution was stirred for 3.5 h. The resultant mixture was added drop-wise in a period of 10 min to 3.63 g allyl chloride. The mixture was stirred for 1 h. Subsequently, THF was removed in vacuo. The crude $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$ was extracted

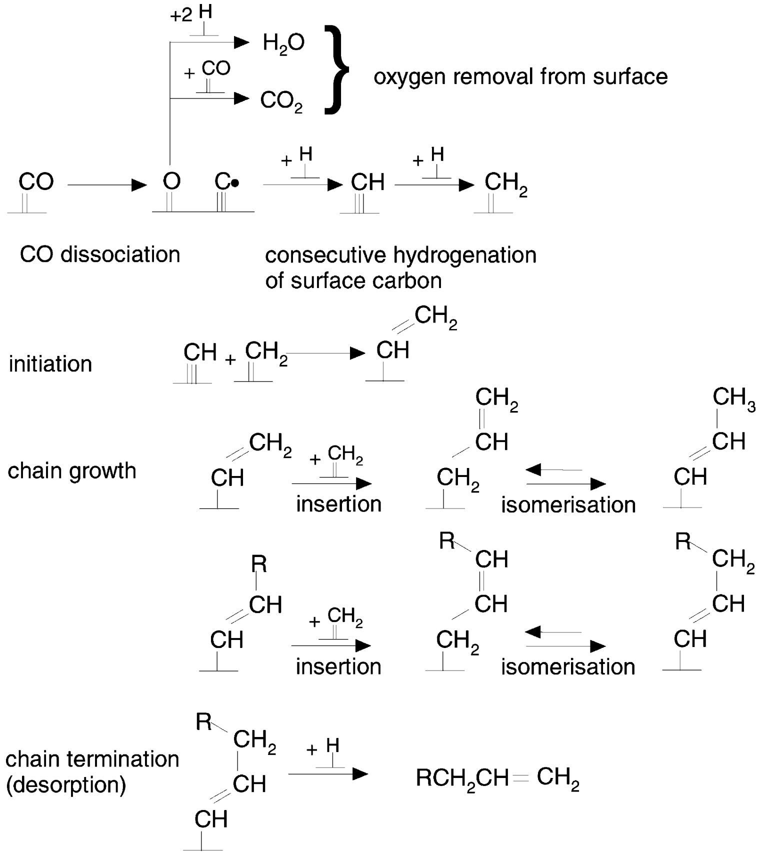

Fig. 2. The alkenyl chain growth mechanism in the Fischer–Tropsch synthesis according to Maitlis et al. [13] as summarised by Moss and co-workers [14].

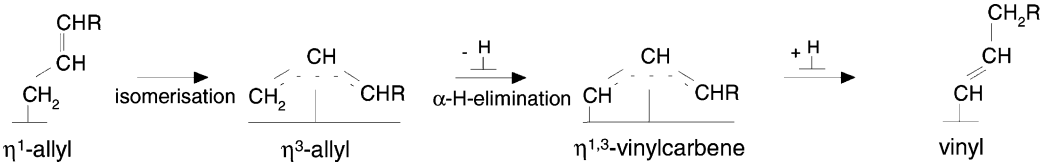

Fig. 3. Proposed allyl–vinyl isomerisation mechanism according to Maitlis et al. [18].

with *n*-hexane. The product was separated chromatographically on a neutral alumina column. The product was obtained by removal of the eluent in vacuo.[1]

*Synthesis of allyl cyclopentamethyl dicarbonyl iron, Fe{[η^5-$C_5(CH_3)_5$]$(CO)_2CH_2CH=CH_2$},**2**.* Fe{[η^5-$C_5(CH_3)_5$]$(CO)_2CH_2CH=CH_2$}, **2** was synthesised using a similar procedure as for the synthesis of **1**. A solution of cyclopentamethyl dicarbonyl iron dimer, (Fe{[$C_5(CH_3)_5$]$(CO)_2$})$_2$ in THF was then added to the sodium amalgam solution. The crude Fe{[η^5-$C_5(CH_3)_5$]$(CO)_2CH_2CH=CH_2$} was extracted with

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[1] Fe{[η^5-C_5H_5]$(CO)_2CH_2CH=CH_2$}, **1**—amber coloured oil at room temperature, IR (*n*-hexane) ν_{CO}: 2012 cm^{-1}(s), 1960 cm^{-1}(s), ^{1}H-NMR ($CDCl_3$): σ_H 2.11 ppm (2H, d, –CH_2–), 4.69 ppm (5H, s, C_5H_5), 4.58–4.76 ppm (2H, dd, =CH_2), 6.04 ppm (1H, m, –CH=).

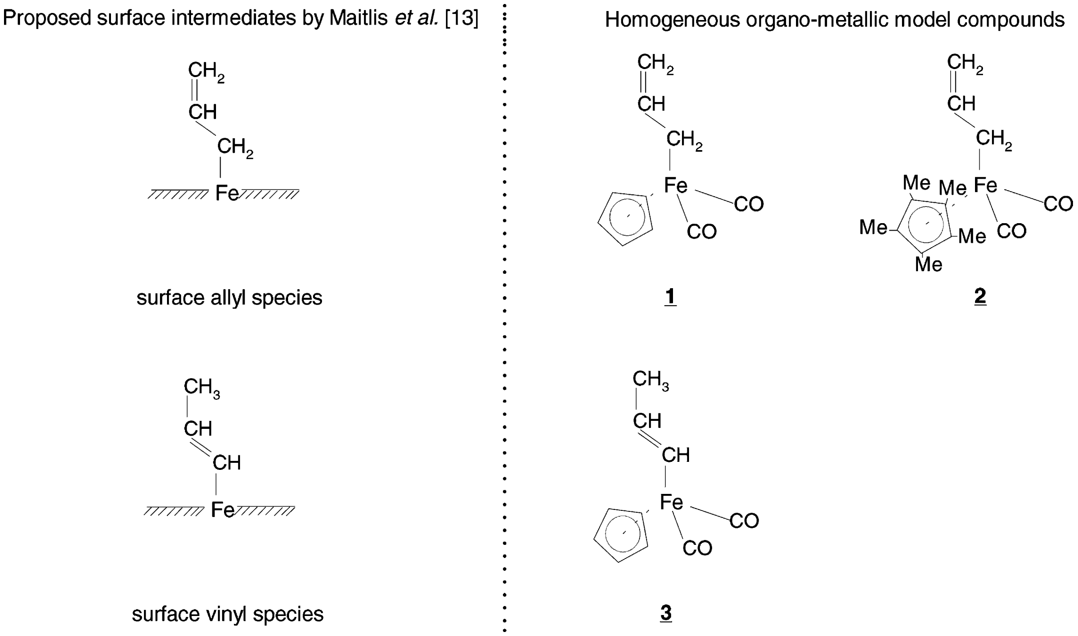

Fig. 4. Proposed surface intermediates by Maitlis et al. [13] and the model compounds used in this study.

n-hexane. The solvent was removed in vacuo yielding the yellow orange crystalline solid.[2]

Synthesis of vinyl cyclopentadienyl dicarbonyl iron, $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH{=}CH\text{–}CH_3\}$*,* **3***.* $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH{=}CH\text{–}CH_3\}$, **3** was synthesised using a continuation of the procedure followed by Quinn and Shaver.[1] 0.711 g $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CO{=}CHCHCH_3\}$ (prepared by a modification of the procedure proposed by Quinn and Shaver [20][3]) dissolved in 100 ml acetone was irradiated with UV for 3 h. The removal of the acyl group was monitored using IR. Acetone was removed in vacuo. The residue was chromatographically separated using deactivated, neutral alumina with n-hexane as eluent. The product was obtained by removal of the eluent in vacuo.[4]

2.2. Thermal conversion of model compounds in inert atmosphere

The possible isomerisation of allyl cyclopentamethyl dicarbonyl iron and vinyl cyclopentadienyl dicarbonyl iron was investigated thermally. The thermal conversion of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$,

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[2] $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**—yellow orange crystals, $T_{\text{melt}} = 82\text{–}87\,^\circ C$, IR ($n$-hexane) ν_{CO}: 1993 cm^{-1}(s), 1941 cm^{-1}(s), ^{1}H-NMR ($CDCl_3$): σ_H 1.73 ppm (15H, s, $C_5(CH_3)_5$), 4.50 ppm (2H, dd, –CH_2–), 4.79 ppm (2H, d, =CH_2), 6.10 ppm (1H, m, –CH=).

[3] $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2COCH{=}CH\text{–}CH_3\}$ was prepared by a modification of the procedure proposed by Quinn and Shaver [20]. A sodium amalgam solution was prepared by stirring 78.3 g mercury with 0.951 g sodium for 5 min. 1.63 g cyclopentadienyl dicarbonyl iron dimer, $(Fe\{C_5H_5(CO)_2\})_2$ dissolved in 10 ml THF was added. The solution was stirred for 1.5 h. The resultant mixture was added drop-wise in a period of 10 min to 1 ml *trans*-crotonyl chloride and stirred for 17 h. THF was removed in vacuo. The crude $Fe\{[\eta^5\text{-}C_5H_5](CO)_2COCHCHCH_3\}$ was filtered through a short silica column with CH_2Cl_2 as eluent. The product was obtained by removal of the eluent in vacuo [18]. $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2COCH{=}CH\text{–}CH_3$—orange-yellow coloured oil at room temperature. Crude-IR (n-hexane): 2054(w), 2024(s), 1965(s), 1931(vw), 1794(w), 1732(vw), 1706(vw), 1657(w)[C(O)R], 1610(w). Crude ^{1}H-NMR ($CDCl_3$): σ_H 1.73 ppm (3H, d, –CH_3), 4.87 ppm (5H, s, C_5H_5), 6.05 ppm (2H, m, CH=CH). Small peaks at 1.90(m). 4.76(s), 5.30(s) and 6.40(d).

[4] $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH{=}CH\text{–}CH_3\}$, **3**—amber coloured oil at room temperature, IR ν_{CO}: 2022 cm^{-1}(s), 1970 cm^{-1}(s), ^{1}H-NMR ($CDCl_3$): σ_H 1.81 ppm (3H, d, –CH_3), 4.79 ppm (5H, s, C_5H_5), 5.56 ppm (1H, m, –CH=), 6.30 ppm (1H, d, –CH=). Unidentified peaks at 1.53 and 4.15 ppm.

1, was studied using IR. The complex was dissolved in *n*-hexane (30 mg/ml) and the solution was transferred to a Schlenk tube previously flushed with nitrogen. The tube was placed in a thermostatic bath at 50 °C.

The thermal conversion of model compounds **2** and **3** was investigated using ^{1}H-NMR. A solution of the model compounds in $CDCl_3$ (5 mg/ml) was prepared. The solution was sealed in an NMR tube previously flushed with nitrogen. The NMR tube was placed in a thermostatic bath at 50 °C.

2.3. Conversion of model compounds in hydrogen atmosphere

Hydrogen plays a crucial role in the isomerisation scheme proposed by Maitlis et al. [18] (see Fig. 3). The conversion of the model compounds was therefore studied in the presence of hydrogen and a hydrogenation catalyst. The model compound was dissolved in methanol (2 mmol/l) and transferred to a conical flask charged with 10 wt.% Pd/C (ca. 0.3 mmol compound/$g_{catalyst}$). The reaction mixture was stirred in a hydrogen atmosphere at room temperature ($p_{H_2} = 1$ atm). The progress of the reaction was followed using IR and ^{1}H-NMR. After hydrogenation, the solvent was removed in vacuo. The residue was filtered through cotton wool using *n*-hexane, which was removed in vacuo.

3. Results

In agreement with other researchers [19], it was observed that $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**, decomposed easily to $(Fe\{[C_5H_5](CO)_2\})_2$. The complex with the pentamethyl cyclopentadienyl ligand $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**, was found to be more stable.

3.1. Thermal conversion of model compounds in inert atmosphere

The IR spectrum did not change during the thermal conversion of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**, with *n*-hexane as a solvent. A precipitate, possibly $(Fe\{[\eta^5\text{-}C_5H_5](CO)_2\})_2$, was formed. The thermal conversion of $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**, in $CDCl_3$, the NMR spectrum did not change, although the intensity of the bands decreased. The initial yellow solution turned dark brown due to the formation of a black precipitate, possibly $(Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2\})_2$. The thermal conversion of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH{=}CH\text{–}CH_3\}$, **3**, in $CDCl_3$ resulted in an increase in the complexity of the NMR spectrum. None of the observed bands, however, corresponded to $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**, instead a decomposition to the dimer and hydrocarbons could have occurred.

The isomerisation of the allyl compounds **1** and **2** to a vinyl compound and the isomerisation of the vinyl compound **3** into the allyl compound **1** could not be observed in an inert atmosphere. The favoured reaction pathway observed under the chosen reaction conditions was the decomposition to the dimer. Assuming first-order kinetics, the rate constant for the decomposition of model compounds **1** and **2** were estimated (see Table 1). The rate constant of the decomposition clearly indicates the lower stability of model compound **1** in comparison to model compound **2**.

3.2. Conversion of model compounds in hydrogen atmosphere

^{1}H-NMR spectra of the product of the conversion of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**, in a hydrogen atmosphere, measured in $CDCl_3$, showed new CH_2

Table 1
Rate constants for the decomposition of the allyl compounds **1** and **2** in inert atmosphere at 50 °C

	Compound	
	$Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**	$Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**
Product	$(Fe\{[\eta^5\text{-}C_5H_5](CO)_2\})_2$	$(Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2\})_2$
Solvent	C_6H_{14}	C_6D_6
k (h^{-1})	>4.0	0.45

Table 2
Rate constants for the conversion of the model compounds at room temperature in hydrogen atmosphere in the presence of Pd/C

Compound	k (h^{-1})
$Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**	~2
$Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**	>4.0
$Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH{=}CHCH_3\}$, **3**	0.007

and CH_3 bands (σ_H of 1.32 and 0.93 ppm, respectively) suggesting the formation of an alkyl species. The integration was, however, not consistent with the formation of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH_2CH_3\}$ [21]. The position of the CO band in the IR spectrum remained unchanged at 2012 and 1961 cm^{-1}, but the intensity of the band was decreasing with reaction time. This implies that the hydrogenation product had no CO ligands.

Hydrogenation of $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**, goes to completion quickly. ^{1}H-NMR spectrum of the product did not show the characteristic bands due to $–CH_2–$, $–CH=$ and $=CH_2$ of the allyl ligand. The spectrum suggested the formation of $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH_2CH_3\}$ [22].

In contrast, the hydrogenation of $Fe\{[\eta^5\text{-}C_5H_5](CO)_2\ CH{=}CH{–}CH_3\}$, **3**, is rather slow (see Table 2). After 50 h under hydrogen, only ca. 30% of the starting complex had reacted. ^{1}H-NMR and IR bands, which could be assigned to the expected hydrogenation product $Fe\{[\eta^5\text{-}C_5H_5](CO)_2\ CH_2CH_2CH_3\}$ were observed.

4. Discussion

The use of metallo-organic model compounds to test possible reaction pathways in the Fischer–Tropsch synthesis is limited due to the limited stability of these complexes. Conclusions from such study have their validity, if it can be assumed that the chemistry of the metal–carbon bond is not significantly different in the metallo-organic complexes and for the surface species in the heterogeneous catalysed Fischer–Tropsch synthesis.

A further limitation of this study is the use of mono-nuclear complexes. The Fischer–Tropsch synthesis is known to be a structure-insensitive reaction [23], i.e. the rate of reaction is independent of the size of the metal particle, on which the reaction takes place. This would principally mean that each of the irreversible reaction steps should take place on a single site, and thus also the allyl–vinyl isomerisation.

The conversion of the allyl compounds **1** and **2** was under all conditions tested more rapidly than the conversion of the vinyl compound **3**. This implies that the vinyl species are more stable than allyl species. Li and Turnbull [24] indicated that allyl complexes can undergo decomposition through radical intermediates. It might thus be expected that even under Fischer–Tropsch conditions the vinyl species would be more stable than the allyl species. Therefore, the isomerisation of an allyl species into a vinyl species, which is required according to the mechanism proposed by Maitlis et al. [13], should be favoured, if a reaction pathway between these species exists.

The conversion of the allyl to the vinyl species was, however, not observed. This is in accordance with observations by others [19]. This indicates that the isomerisation on a model site as used in this study is not feasible. The favoured reaction pathway seems to be cleavage of the metal–carbon bond, or homolytic fission. Even the reaction under UV radiation (not reported here, see also [25]) does not lead to the vinyl product, but lead to the decarbonylated product $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)\pi\text{-}CH_2{=}CH{=}CH_2\}$. The subsequent reaction step leading to the vinyl species is then, however, not observed.

In the reaction scheme for the isomerisation of allyl to vinyl species (see Fig. 3) proposed by Maitlis et al. [18], surface hydrogen is necessary. At room temperature in the presence of hydrogen, but without an additional hydrogenation catalyst, a conversion of $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**, was not observed. In the presence of a hydrogenation catalyst (Pd/C) $Fe\{[\eta^5\text{-}C_5H_5](CO)_2CH_2CH{=}CH_2\}$, **1**, was readily converted to $(Fe\{[\eta^5\text{-}C_5H_5](CO)_2\})_2$ and some unidentified hydrocarbons. $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH{=}CH_2\}$, **2**, is more stable against the metal–carbon bond cleavage and hydrogenation of the allyl ligand is observed with $Fe\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2CH_2CH_2CH_3\}$ as the product. The isomerisation of the allyl compounds **1** and **2** into vinyl compounds was not observed. It can thus be concluded that allyl species under Fischer–Tropsch conditions will readily be hydrogenated or undergo metal–carbon bond cleavage, if the allyl species exist under Fischer–Tropsch conditions.

Also, the vinyl model compound **3**, Fe{[η^5-C_5H_5] $(CO)_2CH{=}CH{-}CH_3$}, is hydrogenated to the corresponding alkyl compound, Fe{[η^5-C_5H_5]$(CO)_2$ $CH_2CH_2CH_3$}, albeit much slower than the allyl model compounds. Again, the isomerisation of the vinyl into the allyl species was not observed. The slower hydrogenation of the vinyl double bond in comparison to the allyl double bond can be explained in terms of accessibility to the active sites for hydrogenation. In this study, the active site for hydrogenation were supplied externally.

5. Conclusions

The mechanism proposed by Maitlis et al. [13,18] was investigated in depth. Their mechanism can principally not explain the full mechanism of the Fischer–Tropsch synthesis, since it predicts a primary olefin selectivity of 100 mol%, which is not observed experimentally.

In order to study the feasibility of the proposed mechanism, the key step, the allyl–vinyl isomerisation, was studied using metallo-organic model compounds with allyl and vinyl ligands. Upon heating in an inert atmosphere, the complexes decompose. The allyl–vinyl isomerisation was not observed. In the presence of hydrogen and a hydrogenation catalyst, the hydrogenation of the ligands or the cleavage of the metal–carbon bond could be observed. Also under these conditions, the allyl–vinyl isomerisation was not observed.

It can thus be concluded that if allyl and vinyl species exist under Fischer–Tropsch synthesis conditions, those species would desorb or be hydrogenated to alkyl species. The allyl–vinyl isomerisation has never been observed experimentally. The isomerisation of the allyl species seems to proceed to a $\eta^{1,3}$-vinylcarbene species and not to a vinyl species. Therefore, the contribution of the mechanism proposed by Maitlis et al. [13] does, in our opinion, not contribute to the chain growth mechanism in the Fischer–Tropsch synthesis.

Acknowledgements

Financial support from SASOL, NRF and THRIP is gratefully acknowledged.

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