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THE MECHANISM OF CHAIN GROWTH IN THE FISCHER-TROPSCH HYDROCARBON SYNTHESIS

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It is proposed that the slow step in chain growth during the Fischer-Tropsch hydrocarbon synthesis is the formation of an adsorbed ethylidene species from two adsorbed methylenes. Addition of a further methylene species gives a diadsorbed C_3H_6 entity, which leads to a singly attached carbonium ion. A 1,2 hydrogen shift then forms a methyl substituted ethylidene species, which is available for further polymerisation. Further hydrogen shift may occur, yielding an olefin and terminating the chain growth. The extent of chain branching is dictated by the relative stability of secondary and primary carbonium ions, as previously proposed by McCandlish, (J. Catalysis 83 (1983) 362).

1. Introduction

The mechanism of the Fischer-Tropsch hydrocarbon synthesis continues to arouse considerable academic interest. It is now generally agreed that carbon monoxide dissociation is an important early step on active FT catalysts such as iron, cobalt and ruthenium [1]. Controversy still remains as to the mechanism of the chain growth. The proposal of Brady and Pettit [2], in which a bond is formed between adsorbed methyl and methylene species, has generated a lot of interest. It offers, however, no clear explanation of the branching ratios in the FT product mixture and it also appears inconsistent with recent transient kinetic studies, which we regard as extremely significant. Mims et al. have studied the chain growth on cobalt, iron and ruthenium catalysts, [3,4]. Their results on the first two metals indicate that the number of growing chains is small, but that, once a C_2 entity is formed at the surface, growth is very rapid. On ruthenium there is evidence that the C_2 species is of different stability to C_3 and longer chains [4]. Detailed product analysis also showed that, in contrast to the McCandlish mechanism, the monomer units add only at one end of the growing chain.

The importance of the C_2 species is also central to a mechanistic proposal due to McCandlish [5] which was principally designed to explain the relatively small but constant ratio of branched hydrocarbons formed during the reaction. This mechanism suggested that the C_2 species is a surface vinylidene, which reacts with adsorbed methylene to give a *cyclo*propylidene. The success of this mechanism in giving a quantitative explanation of branching was described by Anderson et al. as outstanding [6]. Its credibility has, however, been severely damaged by an organometallic study of Hoel et al. [7–9]. These workers showed that a di-iron cyclopropylidene complex, which accurately models the McCandlish proposal, decomposes to yield allene and not the vinylidene entity required by the McCandlish mechanism.

The most recent mechanistic proposal is due to Maitlis et al. [10], who suggest the importance of an adsorbed vinyl species, ($CH_2=CH{-}M$), formed by the reaction between an absorbed methylene and a methyne species. The vinyl reacts with another adsorbed methylene to give a surface δ-allyl, ($CH_2=CH{-}CH_2{-}M$), which undergoes 1,3 hydrogen migration to form a surface alkenyl. It is argued that this hydrogen shift may occur spontaneously or may require assistance from a Bronsted acid site on the supporting oxide.

Our purpose in this paper is to propose a mechanism which we believe is more consistent with all the available evidence, including what is known, from surface science studies, about the stability of C_2 entities at metal surfaces.

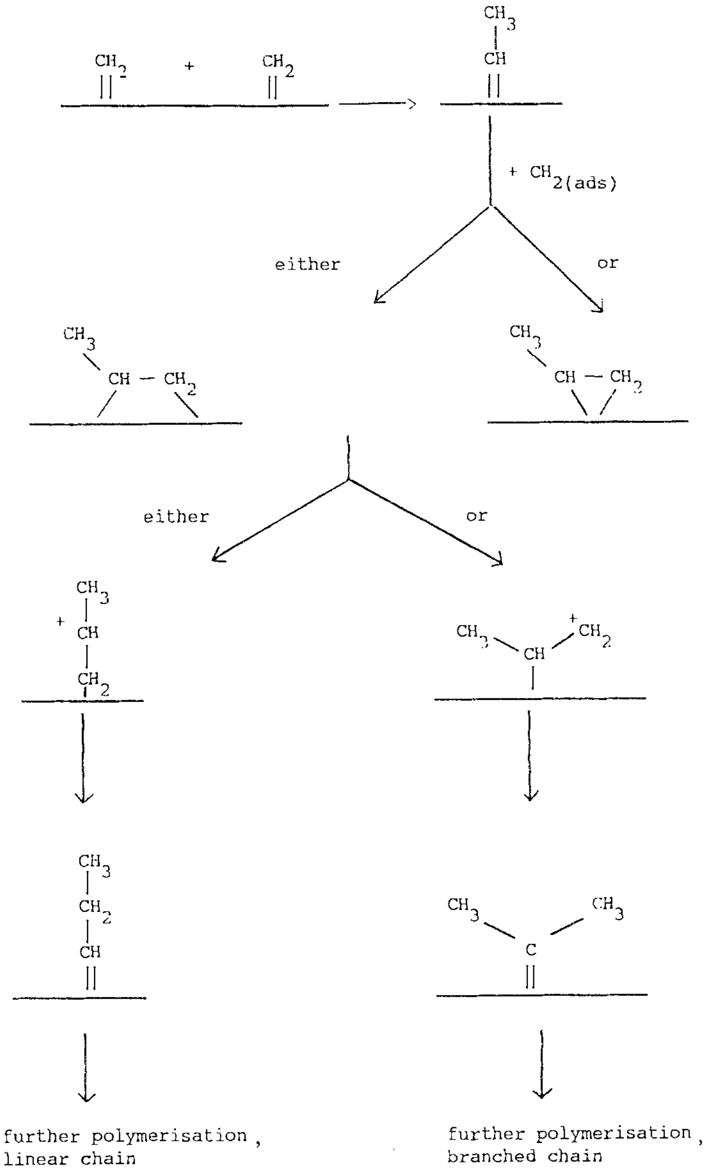
2. Mechanistic proposal

The proposed mechanism is indicated in the Scheme. The slow step, in conformity with the transient kinetics experiments [3,4], is the formation of a C_2 species, adsorbed ethylidene, from the reaction of two adsorbed methylenes. Subsequent homologation is rapid, involving reaction between the adsorbed ethylidene and a surface methylene, to form a substituted, diadsorbed ethylene entity. This is α, β diadsorbed, but it is unclear whether one or two surface metal atoms are involved. The next stage is a rearrangement to give a carbonium ion, through the heterolytic fission of a metal-carbon bond. The negative charge resulting can be dissipated within the metal, and is not shown. As argued by McCandlish [5], the stability of the carbonium ion formed determines the ratio of branched to unbranched chains, with the greater stability of secondary carbonium ion containing species favouring linear chains. The last step in the cycle is 1,2 hydrogen shift, yielding a substituted, adsorbed ethylidene, ready for further, rapid chain growth. Alternatively, desorption as a terminal olefin may occur.

The proposal is believed to have a number of advantages. It justifies the special role of the C_2 entity, it is in accord with what is known about the stability of relevant species on metal surfaces, it allows McCandlish's argument on branching ratios to be retained, it does not involve any additional surface hydrogen species or interaction with the oxide support and lastly it requires only a single surface monomer unit. The mechanism also conforms to the transient kinetics results in that growth occurs only at one end of the chain.

It seems to us crucial to account for the special role played by C_2 species in the reaction. The transient kinetics experiments clearly suggest that the first C–C bond is difficult to form but, once made, gives a very reactive entity. The

Scheme



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reactivity of methylene species on metal surfaces is not known, however their gas phase reaction is highly exothermic.

The "surface science" information available on the surface reactivity of C_2 species is sparse and unfortunately not obtained on active Fischer-Tropsch metals. However the interaction of ethylene with noble metals is fascinating. At 80 K ethylene is molecularly adsorbed on platinum, but on warming to room temperature the molecule dehydrogenates and transforms to an adsorbed ethylidyne moiety, (CH_3–C M) [11]. This is a stable species until quite high temperature, (> 450 K) when further dehydrogenation and fracture of the C–C bond occurs. A similar reaction occurs between ethylene and other noble metal surfaces and with other terminal olefins and platinum [12]. The nature of the driving force in this rearrangement is not known, but the desire for maximum ligancy of the carbon directly bonded to the metal surface is clear. It seems likely that this tendency will be common to all of the late transition metals, so that it is reasonable to expect similar behaviour with, for example iron and ruthenium.

The species we propose is not an adsorbed ethylidyne. We suggest that hydrogen loss does not occur during the reaction of the two surface methylenes. This seems reasonable for a reaction normally carried out in a high pressure of hydrogen.

There are some similarities between this mechanism and the metallocyclobutane species argued to be involved in catalytic olefin polymerisation and certain hydrogen homologation reactions [13,14]. The metallocycle mechanism, however, offers no account of how the initial C_2 species is formed; nor does it give a convincing account of chain branching.

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References

[1] R.W. Joyner, J. Catalysis 50 (1977) 176; and Vacuum, in press.
[2] R.C. Brady and R. Pettit, J. Amer. Chem. Soc. 102 (1980) 6128; 103 (1981) 1287.
[3] C.M. Mims and L.E. McCandlish, J. Phys. Chem. 91 (1987) 929.
[4] C.A. Mims, L.E. McCandlish and M.T. Melchior, Catalysis Letters 1 (1988) 121; and *Proc. 9th Intern. Congr. Catalysis*, ed. M.J. Phillips and M. Teirnan (pub. Chem. Inst. of Canada, Ottawa, 1988) pp 1992.
[5] L.E. McCandlish, J. Catalysis 83 (1983) 362.
[6] C.B. Lee, E.M. Calverley and R.B. Anderson, j. Catalysis 92 (1985) 180.
[7] E.L. Hoel, G.B. Ansell and S. Lehta, Organometallics 3 (1984) 1633.
[8] E.L. Hoel, G.B. Ansell and S. Lehta, Organometallics 5 (1986) 585.
[9] E.L. Hoel, Organometallics 5 (1986) 587.
[10] P.M. Maitlis et al., to be published.
[11] H. Ibach and S. Lehwald, J. Vac. Sci. Technol. 15 (1978) 407.
[12] P.D.A. Pudney, personal communication.
[13] see the discussion given by J.J. Rooney and A. Stewart, in: *Catalysis*, Vol. 1, ed. C. Kemball (pub. Chemical Society, London 1977) pp 277.
[14] C.O'Donohoe, J.K.A. Clarke and J.J. Rooney, JCS. Faraday 1, 76 (1980) 345.