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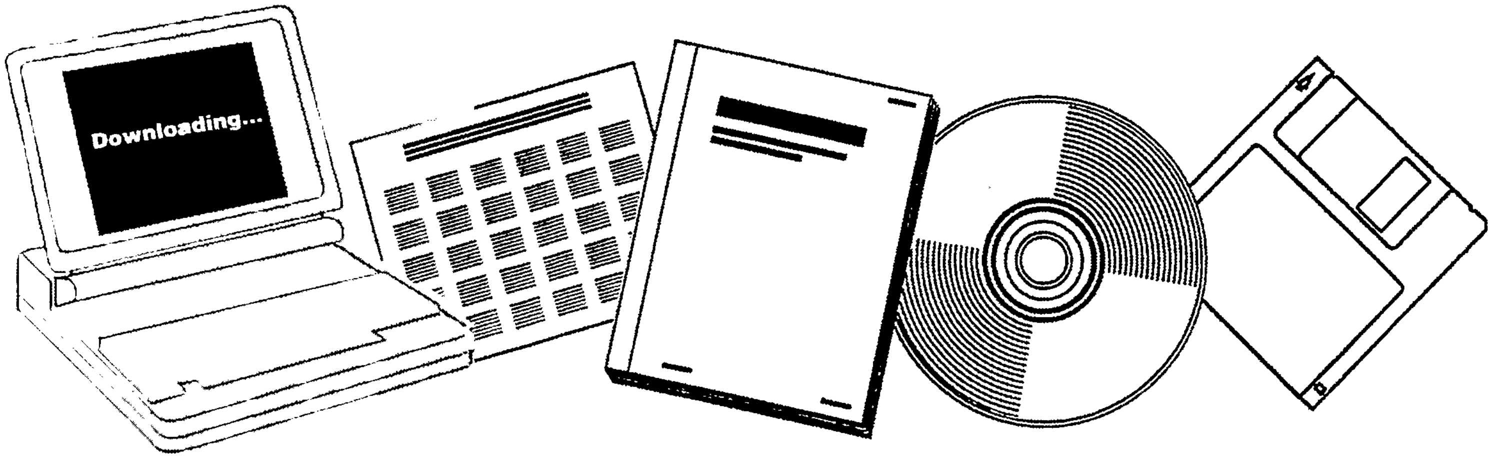

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# KINETICS AND SELECTIVITY IN THE FISCHER-TROPSCH SYNTHESIS

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# KINETICS AND SELECTIVITY IN THE FISCHER-TROPSCH SYNTHESIS*

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The selectivity of the Fischer-Tropsch syntheses is determined by the relative rates of chain lengthening reactions and of reactions which terminate chain growth. Chain lengthening reactions are now generally believed to proceed through adsorption, dissociation and reduction of carbon monoxide to a methylidene group (=$CH_2$) on the catalyst surface. The methylidene group is then incorporated into a growing hydrocarbon chain which may desorb as an olefin or be reduced by hydrogen to a paraffin compound.

Because carbon monoxide dissociation and reduction appears to dominate the overall course of the Fischer-Tropsch synthesis, studies of the reactions of intermediates which relate to selectivity have been sparse. The present work reports the occurrence of olefin homologation on an iron catalyst and discusses possible application to studies of selectivity in the Fischer-Tropsch synthesis.

Added olefins have been frequently used in studies of the course of the Fischer-Tropsch synthesis.(1) Generally, the results of these studies have been to add support for mechanistic descriptions of the synthesis which involve carbidic rather than oxygenated intermediates. More direct support for the involvement of the methylidene group was provided by the work of Brady and Pettit,(2) who used diazomethane as a source of methylidene groups in a study of product distribution and in a study with isotopically enriched carbon monoxide. However, the route by which insertion occurs of methylidene or other surface bonded groups into growing chains is not yet established. Table I lists some of the reactions associated with olefins as related to the Fischer-Tropsch synthesis.

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Olefins have been reported as homologating to higher molecular weight olefins in the presence of nickel(3) and paraffins through assumed olefin intermediates have been reported to homologate on tungsten films.(4) We have found no report of this reaction as being catalyzed by iron in the literature. An example, however, has been found of pentane producing benzene on Rh and Rh-Cu alloy films,(5) which process indicates the occurrence of homologation followed by dehydrocylization. In the course of this work, we have observed similar reactions of olefins on iron.

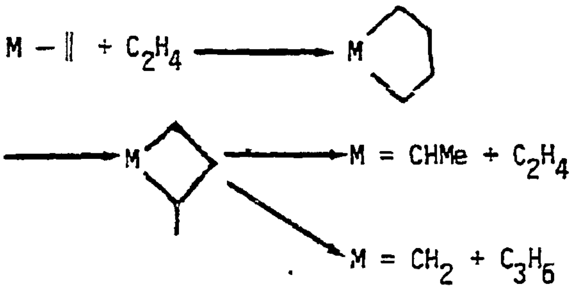
In the descriptive chemistry of some coordination complexes and mono-nuclear compounds of silicon, homologation reactions are commonly reported. Although it is not certain that the chemistry of complex compounds or cluster compounds have a significant relationship to the heterogeneously catalyzed Fischer-Tropsch reaction occurring on a surface, the case for the validity of the analogy has been strongly made.(6) Methylidene insertion has been reported into coordination complexes of nickel, platinum, tungsten, and tantalum,(7) as well as into Si-H and Si-R bonds of silanes.(8) Two reports have been found of homologation by methylidene insertion in iron complexes.(9) Supported iron clusters have been reported as active Fischer-Tropsch catalysts.(10) The fact that similar insertion reactions occur on solid iron catalysts, clustered iron catalysts, and coordination complexes including iron and other metals provides evidence that a common mechanism for insertion may exist.

In this work we used a plug flow reactor containing a commercially available iron oxide catalyst. The apparatus was designed to permit analyses to be made of products using an on-line mass spectrometer. In the study of homologation, after catalyst reduction with hydrogen various olefins were injected into the hydrogen stream and allowed to flow through the reactor. Hydrogenation of the injected olefins competed with homologation to form higher olefins. The higher molecular weight olefins were themselves reduced to paraffins in each injection. From 1-butene as an example isobtained butane and the homologated products pentane, hexane, and octane. The extent of homologation relative to hydrogenation varied with the hydrogen partial pressure (which determined the hydrogen/butane ratio, space velocity, and temperature). Figure (1) shows the homologation of butene-1 to pentene as a function of space velocity at two temperatures. The homologation is measured as the ratio of pentane to butane formed in the competing reactions. The increase of homologation with space velocity implies the existence of a mass transfer effect resulting in an enhanced hydrogen-olefin ratio in the catalyst pores. We take these results to mean that homologation occurs at a rate comparable to that of hydrogenation and perhaps higher.

The temperature variation of homologation is shown in Fig. (2) and indicated an apparent energy of activation about 10 kcal/mole (40 kJ/moles) greater than that for hydrogenation. The occurrence of homologation by more than one carbon atom is indicated by experiments in which the amount of two-carbon atom chain lengthening is compared to chain lengthening by one carbon atom for different isomers of butene. Table II shows the yield of butene homologated with one carbon atom for three isomers and the yield of homologated product showing two carbon atom addition. In both cases the product was reduced to the paraffin and detected as such.

The single carbon atom addition does vary with the state of catalyst carburization, but we believe the differences shown to be representative of reactivity differences between the isomers. Since the single homologation occurs in competition with hydrogenation, the relative yields of single homologation would reflect the differences in intermediate reactivity for homologation if the intermediate were common to hydrogenation as well as homologation. The doubly homologated species as a fraction of the singly homologated product, shown in the final column of Table II shows that for trans-2-butene a larger relative amount of two-carbon atom chain lengthening occurs than for the other two isomers. This result indicates that trans-2-butene can homologate with the addition of a two-carbon atom group.

Although no other data has been found bearing on the intermediates of the heterogeneously catalyzed homologation, we may turn to some of the speculations advanced for coordination compounds. Sumner(9b) postulates a di-iron five membered ring in an ethylene insertion reaction into a methylidene-iron bond, which then rearranges with hydrogen transfer and elimination. McLain, Sancho, and Schrock(11) speculate based on their work with tantalum complexes that alkylidene ligands can form from olefins with incidental formation of homologated olefin. With ethylene, for example,



Although it is premature to relate the homologation reaction to the course of the Fischer-Tropsch synthesis the similarities of the reactions are striking. It is not implausible that we are examining aspects of a reaction which shares common intermediates with the Fischer-Tropsch synthesis.

Hughes and others in their work on supported iron clusters(10c) have proposed a metallo-cyclobutane intermediate for the Fischer-Tropsch synthesis. This type of intermediate could undergo the reactions involving rearrangement, hydrogenation, or decomposition. The relative rates of these reactions would determine the product selectivity. Studies using the homologation reaction reported here offer the possibility of determining with greater precision the chemical behavior of the proposed intermediates.

Numerous proposals have been made for the mechanism of the methylidene insertion reaction. The original proposal of Fischer and Tropsch(12a) involved the association of methylidene groups on the catalyst surface followed by desorption as ethylene, reduction to ethane or association with another methylidene group forming higher homologs. A second proposal type suggests migration of a surface alkyl group to a methylidene species(12b). Hughes et al., as discussed above, proposed a metallocyclobutane intermediate is possible to account for their particular results on small iron particles. Some of the assumptions made in their discussions were that the olefin reaction with surface methylidene was rapid and that small iron particles would have small hydrogenating capabilities. This latter assumption would explain the minimal formation of methane and saturated hydrocarbon reported in their work.

The present work supports the assumption that chain lengthening reactions are rapid and also shows that the hydrogenation of olefins to form paraffins can be minimized by control of the hydrogen pressure. A metallocylcobutane intermediate in the Fischer-Tropsch reaction appears to be plausible.

In conclusion, we have found that olefins homologate on iron catalysts in competition with hydrogenation. Since the homologation reaction occurs to an enhanced extent at lower contact times, it appears to be a fast reaction compared with hydrogenation and may share common intermediates with the Fischer-Tropsch synthesis.

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Table I. Summary of olefin reactions possibly associated with the Fischer-Tropsch synthesis (a,b)

| Name of reaction | Equation |
|---|---|
| I. Hydrogenation | $C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$ |
| II. Chain initiation and growth | |
| (*i*) Activated Adsorption | $C_nH_{2n} + * \rightarrow * - C_nH_{2n-1} + [H]_s$ |
| (*ii*) Methylidene Insertion | $* - C_nH_{2n-1} + [CH_2]_s \rightarrow * - C_{n+1}H_{2n+1}$ |
| (*iii*) Alkylidene Insertion | $* - C_nH_{2n-1} + [CHR]_s \rightarrow * - C_{n+1}H_{2n}R$ |
| III. Incorporation in a growing chain | $* - C_mH_{2m-1} + C_nH_{2n} \rightarrow * - C_{m+n}H_{2m+2n-1}$ |
| IV. Homologation | $C_nH_{2n} \rightarrow C_mH_{2m}$; where m>n (c) |

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[a] $[\ ]_s$ = surface group.

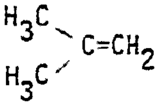
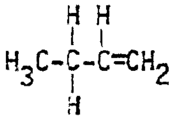
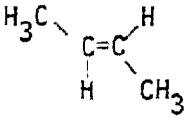
$*$ = specific surface site, one or more atoms.

[b] We assume that a growing chain in the Fischer-Tropsch reaction has the character of a sorbed species, II(*i*)

[c] The source of the additional carbon atoms and other products are not indicated.

Table II

GHSV = 340 $hr^{-1}$; 300°C; $H_2$ at 35 psia (0.25 MPa); olefin/$H_2 \geq 1/2$; at iron

| Injected Compound | Ratio $C_5H_{12}/C_4H_{10}$ (one carbon atom lengthening) | Ratio $C_6H_{14}/C_5H_{12}$ (two carbon atom lengthening) |
|---|---|---|
| <br>Isobutylene | 0.025 | 0.078 |
| <br>$H_3C\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{C}{=}CH_2$<br>1-Butene | 0.014 | 0.057 |
| <br>trans-2-butene | 0.0069 | 0.13 |

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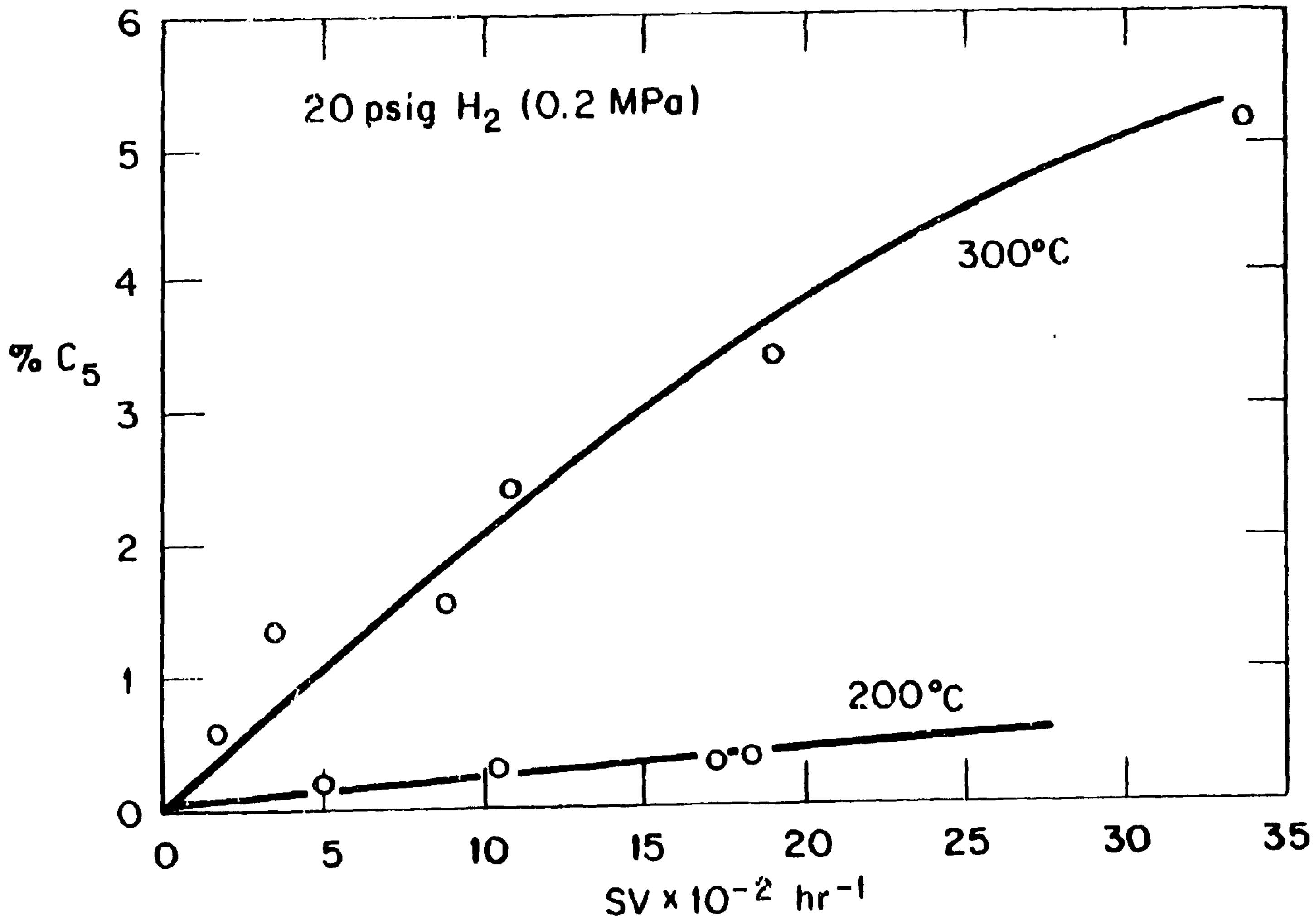

Fig. 1. Extent of homologation of butene-1 to pentene as a function of space velocity.

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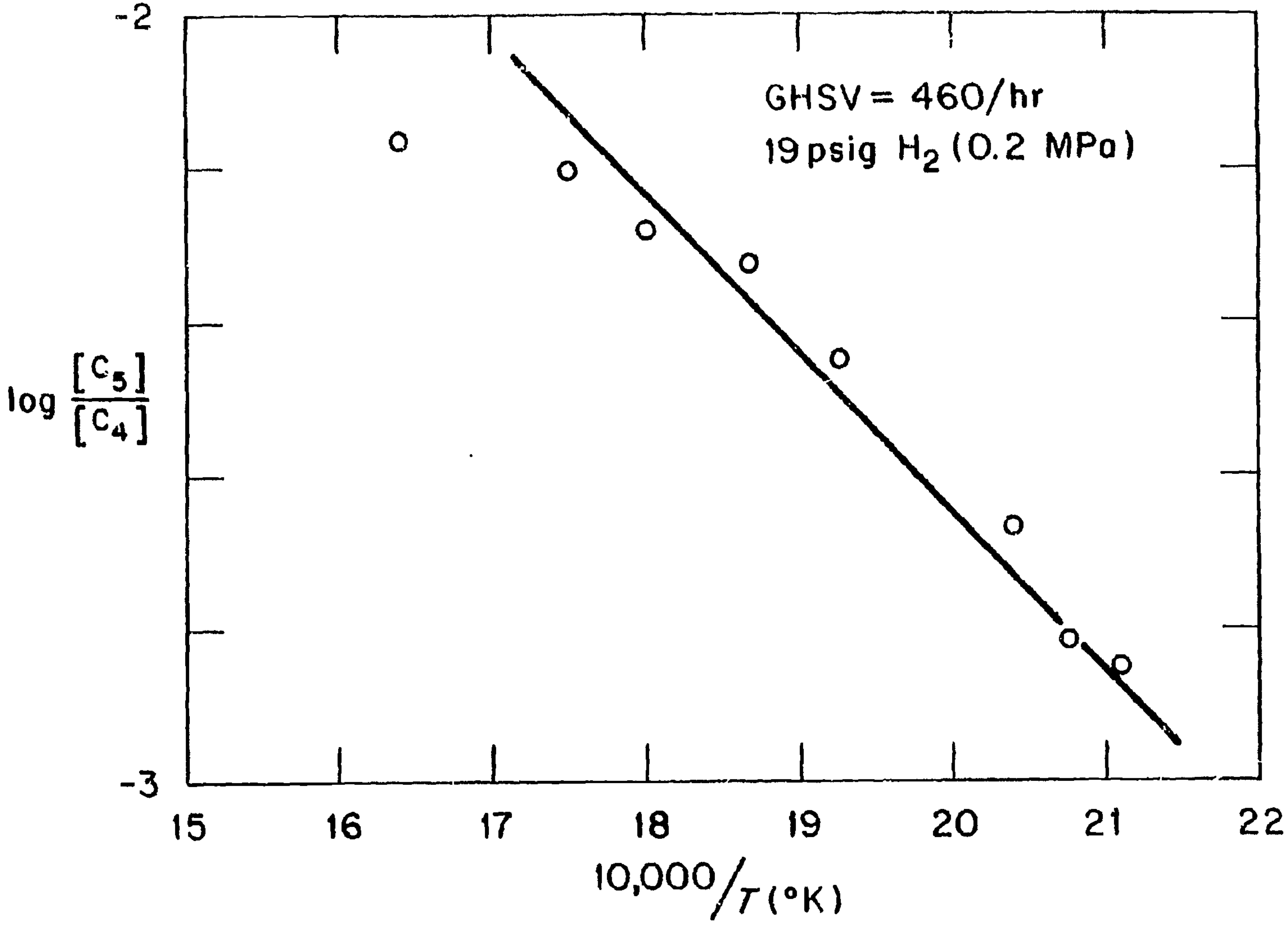
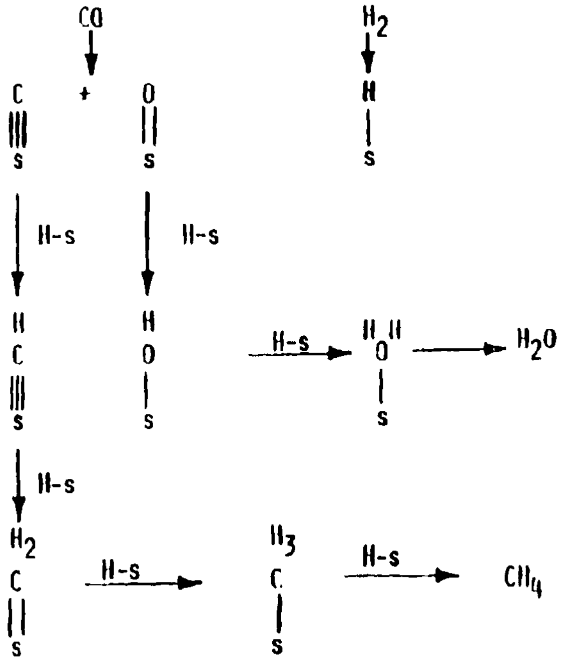
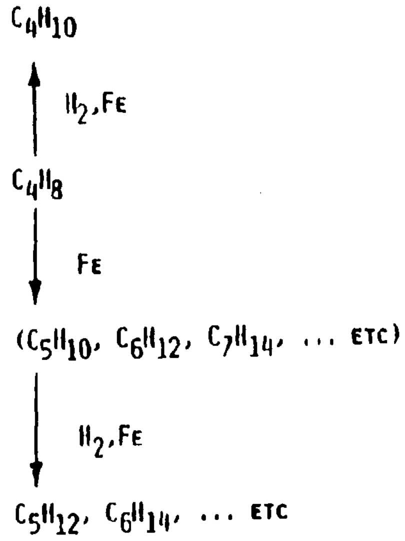


Fig. 2. Temperature variation of homologation relative to hydrogenation.

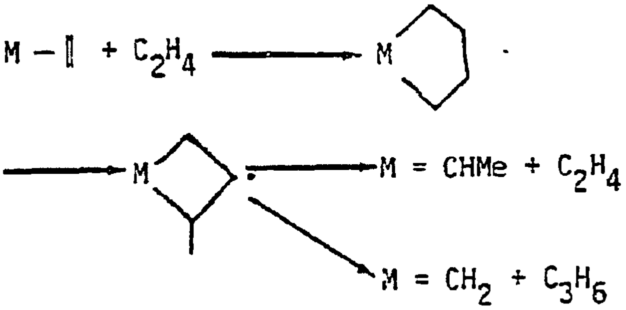
## SCHEME OF INITIAL FISCHER-TROPSCH REACTIONS



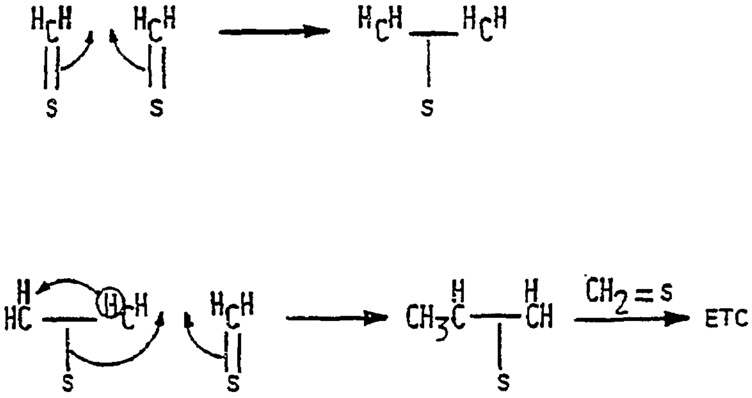
## HOMOLOGATION AND HYDROGENATION OF OLEFINS



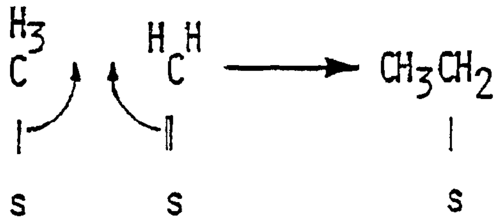
## A MECHANISM FOR HOMOLOGATION



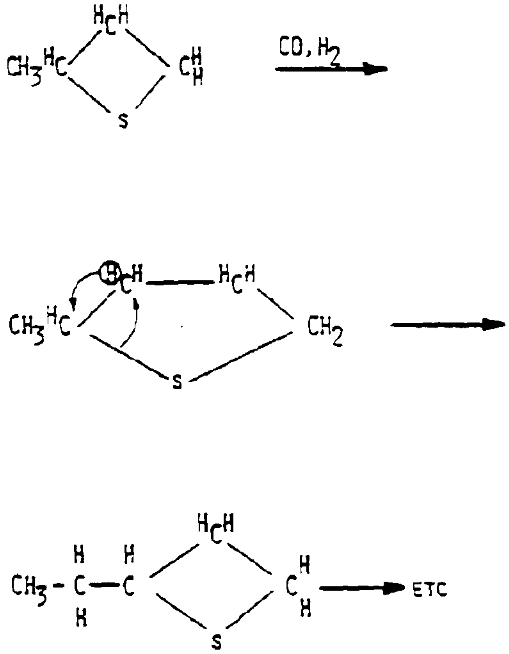
## STEPWISE CHAIN GROWTH MECHANISM



## CHAIN GROWTH BY ALKYL GROUP ADDITION



## CHAIN GROWTH VIA METALLOCYLOBUTANE



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