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New Evidence for the Mechanism of the Fischer–Tropsch Synthesis of Hydrocarbons

HUBERT H. NIJS AND PETER A. JACOBS[1]

Centrum voor Oppervlaktescheikunde en Colloïdale Scheikunde, Katholieke Universiteit Leuven, De Croylaan 42, B-3030 Leuven (Heverlee), Belgium

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New mechanistic evidence is advanced for Fischer–Tropsch synthesis on Ru-loaded Y-type zeolites, Ru-on-silica and Co promoted on kieselguhr. The experiments were carried out in real Fischer–Tropsch conditions, i.e., at high growth rates. Experiments were done in pulse reactors and under transient reaction conditions. ^{13}C-labeled carbon monoxide was used and addition of water and olefins to the synthesis gas was studied. From a series of well-chosen experiments it is deduced that carbon monoxide disproportionation initiates the reaction. Surface carbon is hydrogenated to methane and the reverse water–gas shift reaction accounts for water formation. Water reacts with surface carbon and forms hydroxy-species which initiate chain propagation. The mechanism accounts for a particle size effect and explains why polar conditions stimulate chain growth.

INTRODUCTION

Research on Fischer–Tropsch (FT) synthesis in the early 1970s took off for a new start. The mechanisms proposed in the earlier literature can be reduced to three basic reaction schemes, each supported by considerable evidence. They are commonly referred to as the surface carbide mechanism (*1, 2*), the hydroxy-polymerization mechanism (*3*), and the carbon monoxide insertion model (*4*).

The surface carbide mechanism assumes that dissociative adsorption of CO is the rate-determining step in the hydrocarbon synthesis. The surface carbide is then partially hydrogenated and carbene species are formed which polymerize readily. The hydroxy-polymerization mechanism assumes a –CH_2OH– like surface intermediate which forms higher products by simple condensation. In some cases a surface formyl species is proposed as a reaction intermediate (*5*). Based on the Schulz–Flory distribution of the FT products on some catalysts, the CO-insertion model was developed. It describes chain growth by insertion of CO molecules between the metal surface atom and the first carbon atom of a metal adsorbed alkyl chain. Sometimes it is assumed that alkyl chains migrate on top of adsorbed carbene species (*6*).

During the last few years, many authors have tried to shed new light on the FT mechanism of hydrocarbon synthesis mainly by using techniques which were not available at the time of the earlier polemics on this subject. In this way new evidence has become available which was supporting not only each of the three mentioned mechanisms but even a combination of the carbide and carbon monoxide insertion models (*6–18*).

Araki and Ponec (*15*) gave strong new evidence for the carbide mechanism on nickel and nickel–copper alloys. By using carbon-labeled CO, they found that carbidic carbon could easily be hydrogenated to methane. It was assumed that the same species would easily polymerize to higher hydrocarbons (*13*). The latter hypothesis was confirmed by Biloen *et al.* (*6*) on a

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[1] To whom queries should be sent.

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ruthenium/alumina catalyst with a higher chain growth probability than the nickel-based catalysts. It was shown that labeled surface carbides could be incorporated in hydrocarbon chains containing at least two carbon atoms when nonlabeled reactants were used. Several labeled carbon atoms were found per hydrocarbon molecule. This was considered to be a proof for a polymerization of methylene-like radicals.

Using transient reaction techniques, Matsumoto and Bennett (*9*) have shown that two surface species exist on an iron catalyst. One is very stable and is assumed to be surface carbide. The other could be hydrogenated more readily and was proposed to be an oxygen species. Methanation seemed to occur over the surface carbide, while a CO-insertion mechanism was thought to be responsible for chain growth. In later work, Ponec *et al.* (*14, 19*) recognized the difference between Ru and Ni surface carbides and proposed a hydroxyl-like carbon intermediate for chain growth.

It seems therefore that the controversy on the nature of the intermediate in FT synthesis is still very much alive. A serious drawback in the major part of the experiments reported upon is the non-FT conditions in which they were performed. By this is meant that the chain growth probabilities were not high enough since methane invariably was the major product. This was a result of the use of low reaction pressures and high H_2/CO ratios. Since the selectivity is very sensitive toward reaction conditions and to the nature of the active metal, it remains doubtful whether the phenomena occurring at high growth probabilities remain unchanged at lower growth rates.

Therefore it was thought that mechanistic work in real FT conditions, i.e., at high growth rates, could yield new information on the nature of the surface species. Most of the techniques used have been applied before. They consist of the use of pulse reactors, of transient reaction conditions with labeled molecules, and of the additives water and olefins.

EXPERIMENTAL

Materials. The catalyst supports used were NaY zeolite (Union Carbide, Linde Division), Aerosil-type silica (Degussa), γ-alumina (Ventron) and kieselguhr (KG) (Ventron). $Ru(NH_3)_6Cl_3$ from Strem Chemicals, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $La(NO_3)_3$ from Merck A.G. were used as the starting materials for the catalysts.

The silica- and alumina-based catalysts were obtained by impregnation and contained 3% by weight of Ru. A cobalt-on-KG catalyst was prepared according to established methods (*20*) and contained 30 wt% of Co and K_2O and MnO_2 as promoters.

The zeolite-based catalysts were prepared by ion-exchange using dilute solutions (0.02 *M*) and suspensions (0.02 kg dm^{-3}). The zeolites used were NaY, DB-Y (deep-bed Y) derived from it using known procedures (*21*), and a LaY zeolite prepared by ion-exchange under reflux conditions. The first two zeolites contained 4–9% by weight of Ru, the latter one 2%.

Labeled carbon monoxide (^{13}CO) was from MSD and contained 90% of the heavy isotope. It was diluted with ultra-pure helium (Gardner) to 10% by volume. The other gases used (CO, H_2, Ar, He, 1-butene, and isobutene) (L'Air liquide) had a purity better than 99.99%.

Apparatus. The catalytic experiments were carried out in a high-pressure continuous flow tubular reactor. Sampling was done on-line. The analytical procedure will be published elsewhere (*22*). The use of an internal standard allowed us to make accurate carbon balances. The analysis time for all hydrocarbons up to C_{12} was about 2 hr.

Incorporation of ^{13}C into the Fischer–Tropsch products was investigated using a Hewlett–Packard 5990 GC/MS combination equipped with a 100 m OV-101 capillary column.

Procedures. The standard Fischer–Tropsch conditions used were as follows: CO/H_2 ratio of 2/3; reaction pressure, 14 kg cm^{-2}; contact time, 0.4 sec. Samples taken at short intervals of time were stored by means of a Valco 32-port valve and analyzed afterward. The standard reaction temperature used was 200°C. Experiments with labeled CO were done as follows. The surface of the metal in the catalyst at reaction temperature was completely covered with ^{13}C using the disproportionation of an excess of ^{13}CO. Reaction was carried out with unlabeled reactants and the products condensed in a liquid nitrogen trap for a given amount of time, usually 10 min. The cold trap was then purged with helium so as to remove the last traces of CO in order to avoid mass spectrometric interference with C_2H_4 formed. Blank runs were done in order to be able to correct for naturally occurring ^{13}C in the products and for isotopic scrambling in the mass spectrometer.

High-pressure-pulse experiments were carried out with the high-pressure reactor by means of a six-way sampling valve with a 10 ml loop. The loop contained synthesis gas at a pressure of 11 kg cm^{-2} and this could be brought into the helium flow at the same pressure. It was checked that the shape of the pulse of synthesis gas was almost rectangular. A sample was taken in the middle of this pulse to determine its composition after reaction.

The incorporation of 1-olefins (but-1-ene and methylpropene) was done as follows. The olefin was mixed with the synthesis gas feed, which then contained 3% by volume of the olefin. Reaction occurred at a pressure of 7 kg cm^{-2} and a contact time of 0.8 sec. In some cases water was also added to this feed so as to have 1% in the entrance gas stream. Sampling was carried out after 30 min reaction time.

The powdered catalysts were air-dried, pelletized, crushed, and sieved. The 40–60 mesh size was used for catalytic work. The catalyst (0.6 ml) was diluted with the same volume of quartz of the same average particle diameter and loaded into the reactor. The catalyst was then dehydrated at about 200°C in flowing helium, cooled down, and contacted with hydrogen. Afterward the catalyst bed temperature was gradually increased (100°C/hr) up to a final reduction temperature of 400°C.

The catalyst acidity was measured by hydrocracking *n*-decane at temperatures and pressures similar to the FT conditions. Hydrogenolysis occurs at the Ru surfaces. Cracking occurs via a classical bifunctional mechanism over Ru and acid sites, the transformations over the acid sites being rate limiting. From the conversion and product composition the extent to which the bifunctional mechanism occurs can be easily determined and the materials can be ranked, at least semiquantitatively, according to catalyst acidity.

RESULTS

The Influence of Support Acidity on Hydrocarbon Chain Growth

Dautzenberg *et al.* (*11*) reported that for a ruthenium/alumina catalyst, the hydrocarbon chain growth increased steadily with time until an equilibrium was reached. It was found that one C_1-unit was attached to the growing chain every minute. Our first aim was to investigate systematically the effect of support acidity upon the time at which constant growth rate was reached.

Based on its bifunctional behavior (see experimental section) catalyst acidity was found to decrease in the following order:

$$\text{Ru/DB-Y} > \text{Ru/LaY} > \text{Ru/NaY} > \text{Ru/Aerosil} > \text{Co/Kieselguhr}$$

The last catalyst behaves as a basic solid due to the promoters present. A RuNaY zeolite after reduction of the Ru(III) cations contains an equivalent amount of protons. Figure 1 shows the changes in the chain growth probabilities (α) with the time on stream. α is defined according to Schulz–Flory kinetics:

$$W_n = n(1 - \alpha)^2 \alpha^{n-1}$$

W_n being the weight fraction of carbon number n. While no effect is visible for the basic reference catalyst (Co promoted on

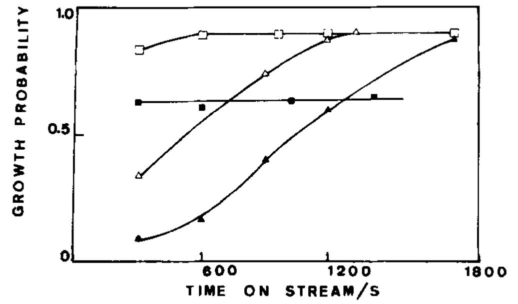


FIG. 1. Change in growth probability (α) of a Fischer–Tropsch synthesis with time on stream. (□) Ru on Aerosil; (△) RuNaY; (▲) RuDB-Y; (■) Co on kieselguhr (promoted).

kieselguhr), an increase of α with time on stream is observed for all other catalysts considered. The growth probability on the Ru-based catalysts tends to a common value of 0.9 independent of the catalyst acidity. This value is obtained more readily for the less-acidic catalysts. The α value for the reference catalyst ($\alpha = 0.63$) is perfectly normal for cobalt in the reaction conditions used. The α value of 0.9 for Ru is also not unexpected.

Once the steady state was reached, the catalysts were hydrogen treated at reaction temperature and the experiment repeated. The phenomena described in Fig. 1 are then shown to be completely reproducible. At the time deactivation starts gradually, the opposite phenomenon is observed: α decreases again with time on stream. During the initial period of the reaction when α grows, the total hydrocarbon yield remains unchanged. In other words, during this period the yield of C_1 decreases gradually while longer hydrocarbons are progressively formed.

It is considered common knowledge that basic supports enhance chain growth (*23*). Nevertheless no attempts have been reported to determine the physicochemical basis of this relation. In an attempt to do so, 1% of water was added to the feed in a standard FT experiment using the acid Ru/DB-Y catalyst. The conversion was not altered within analytical significance but substantial differences in product selectivity were observed. Figure 2 shows the product selectivity ratio obtained in the experiment using wet and dry synthesis gas, respectively. Product sampling was done after 6 min reaction time. It is clear that the addition of steam shifts the product distribution to higher carbon numbers on this acidic support. At the same time, it is found that the growth probability α has almost doubled (from 0.11 to 0.20) in the case of added steam. For the other less acidic catalysts used, α was already at equilibrium after 5 min of reaction time.

Precarbiding of the Metal Surface

The surface carbide theory has been verified experimentally for Ru/alumina catalysts (*6*) using labeled carbon. Unfortunately these experiments were done with an excess of catalyst and an incompletely covered Ru surface. In this way it cannot be excluded that upon reaction other intermediates (e.g., oxygen-containing species) could be formed. Therefore, in the present case it was checked that all carbon was deposited by the Boudouard reaction and as a result no oxygen was left near the surface. Furthermore it was certified that the surface of the metal was completely covered with ^{13}C-labeled carbon.

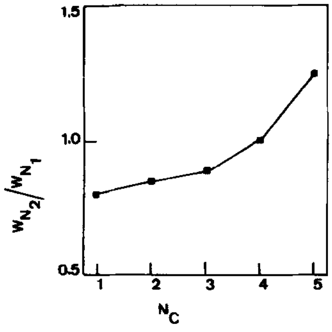


FIG. 2. Influence of the presence of water upon the FT selectivity over RuDB-Y zeolite. The hydrocarbon distribution at different carbon numbers (N_c) in the presence (W_{N2}) of added steam (1% by volume of reactants) is compared to the distribution obtained under standard reaction conditions (W_{N1}).

TABLE 1

Incorporation of Labeled Surface Carbide into FT Products over RuNaY[a]

Product hydrocarbon	$(M + 1)/M \times 100$[b,c]		Percentage increase of $(M + 1)/M \times 100$
	Blank experiment	Labeled surface carbide	
CH_4	1.6	2.4	49
C_2H_6	2.9	2.9	0
C_3H_8	3.2	3.3	3
n-C_4H_{10}	4.1	4.2	2
i-C_4H_{10}	3.8	4.1	7

[a] After 10 min reaction time.

[b] M, Intensity of molecular ion peak.

[c] The error determined for these ratios was ±0.1.

RuNaY zeolite was treated with ^{13}CO so as to obtain a metal surface completely covered with ^{13}C. Unlabeled synthesis gas was used and the products obtained under standard reaction conditions were collected and the distribution of ^{13}C among the products investigated. The results are given in Table 1. It is clear that all carbon deposited on the surface by carbon monoxide disproportionation evolves as $^{13}CH_4$.

From the results presented so far it appears that at the beginning of a FT reaction some surface carbon is formed which is easily hydrogenated to methane but which does not initiate chain growth. Another species is gradually formed later on which can initiate chain growth. The rate at which this species is formed decreases when catalyst support is more acidic. The formation of this second species is enhanced by the presence of water.

Transient Reaction Conditions

In order to clarify the phenomena which occur in the early stage of the FT reaction and to obtain insight into the gradual formation of the postulated two surface species, pulse experiments were carried out in standard reaction conditions. Figure 3 shows the results for Co on kieselguhr and for RuNaY zeolite. Both catalysts behave in the same manner. It should be noticed that the CO conversion remains unaltered during the experiment and is 25 and 35% for the two catalysts, respectively. During the first few pulses, the conversion of CO and the CO_2/CH_4 ratio are at their maximum values. This shows that initially the following reactions occur:

$$2CO \rightarrow C + CO_2 \qquad (1)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (2)$$

which give as overall reaction stoichiometry on a clean metal surface

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad (3)$$

Both the conversion and the selectivity for

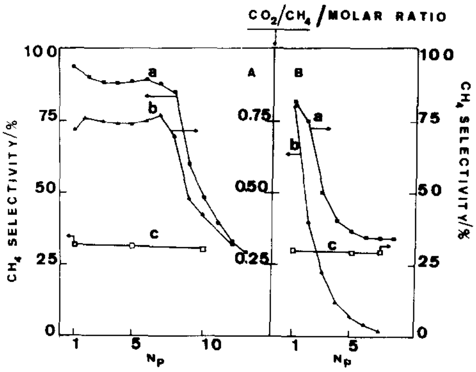


FIG. 3. Methane selectivity (a,c) and CO_2/CH_4 molar ratio (b) at different pulse numbers (N_P) during a FT experiment in the pulse reactor over (A) cobalt promoted on kieselguhr and (B) RuNaY under standard reaction conditions (a,b) or in the presence of added steam (c).

CH_4 and CO_2 then show a very sudden drop. For RuNaY this occurs at the second pulse, for Co on kieselguhr it happens only after admission of nine pulses. This difference is quantitatively related to the available metal surface on an equal amount of catalyst.

All this indicates that at a definite moment a relevant change in the reactive surface species takes place. When 1% of water is added to the synthesis gas feed, the steady-state equilibrium is reached at once (Fig. 3c) and even no traces of CO_2 could be detected. Water again seems to iniatiate the formation of a second surface intermediate which leads to chain growth.

Figure 4 shows how conversion and methane selectivity in a FT synthesis change with time of reaction over RuNaY. During the initiation period high activity and 100% selectivity for CH_4 is obtained. Gradually the conversion drops to a constant level while larger hydrocarbon chains are formed. At constant conversion the product selectivity also gradually comes to an equilibrium. Finally deactivation starts and a new rise in CH_4 selectivity occurs.

Incorporation of 1-Olefins in the Growing Chains

Incorporation of 1-olefins in growing hydrocarbon chains and analysis of the formed products have already proved to be a powerful method to unravel the nature of possible surface structures (*25–27*). In the present work, but-1-ene and methylpropene were used for incorporation over Ru-LaY zeolite and Ru-on-Aerosil. In this way, the chemical structure of the olefin and the acidity of the catalyst was included as a selectivity determining parameter. Also the supplementary addition of steam to these feeds was investigated.

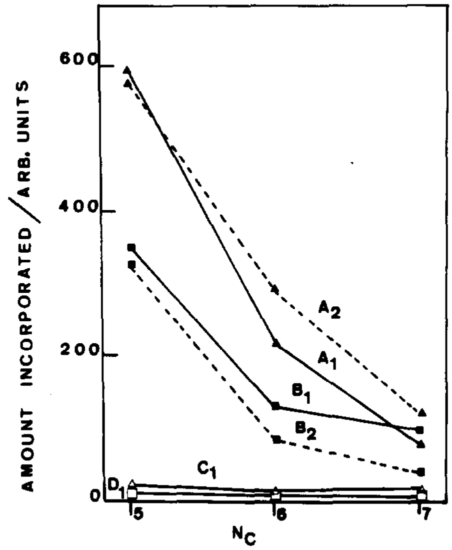


FIG. 5. Incorporation of 1-olefins in different carbon number fractions (N_c) over RuLaY (A and B) and Ru on Aerosil (C). But-1-ene (A_1, A_2, C_1) and methylpropene (B_1, B_2, D_1) under standard conditions (A_1, B_1, C_1, D_1) and with steam added (A_2, B_2).

The selectivity of the olefin reaction pathways is given in Table 2. The incorporation of 1-olefins is significantly higher on the acidic catalysts. In each case the linear olefin is found to be incorporated more easily. It was also found (Fig. 5) that the coaddition of steam has no influence on the amount of olefin incorporated on the Ru-

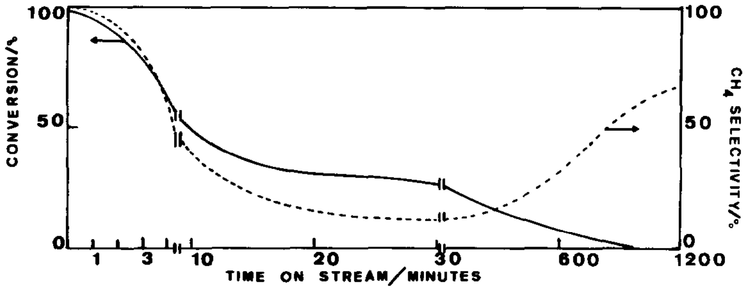


FIG. 4. FT activity and methane selectivity against time on stream over RuNaY.

TABLE 2

Reaction Selectivity[a] of 1-Olefins Added to the FT Feed

Reaction	Ru on Aerosil		RuLaY	
	But-1-ene	Methylpropene	But-1-ene	Methylpropene
Isomerization	56.0	2.1	39.0	0.9
Hydrogenation	6.0	0.9	25.0	40.0
Dimerization	0.0	4.0	0.0	5.4
Incorporation	3.6	2.0	23.0	16.0

[a] wt% of added olefin which has reacted.

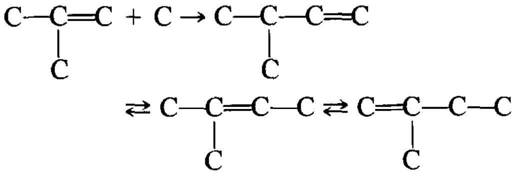
on-Aerosil catalyst. On RuLaY the incorporation of but-1-ene is assisted by the coaddition of water, while the incorporation of methylpropene is inhibited in the same conditions. Figure 5 clearly shows that addition of C_1 species to the C_4 olefins is most abundant, but that C_2 as well as C_3, although in decreasing amounts, can still be added to the chain. In the C_8 fraction the incorporation is negligible in the case that dimerization does not disturb the evaluation of the data (Table 2).

The product distribution for the RuLaY catalyst in the C_5, C_6, and C_7 hydrocarbon fractions indicates that when the two mentioned 1-olefins are added to the synthesis gas, extensive secondary isomerization occurs. Indeed, the paraffins in each hydrocarbon fraction are very close to thermodynamic equilibrium. For the Ru-on-Aerosil catalyst this kind of secondary isomerization is absent as can be seen from the data in Table 3. Indeed, the product distribution clearly proves that the main growth route occurs by "end-to-end attachment." This is substantiated by the following observations:

(i) In the case of but-1-ene incorporation there is an important increase of hex-3-ene and a slight relative growth of c-pent-2-ene and heptane.

(ii) In the case of methylpropene incorporation there is a definite decrease of all linear products, which in its turn shows that secondary isomerization is not present.

(iii) In the case of methylpropene incorporation there is an important increase of 2-methylbut-2-ene and 2-methylbut-1-ene yield. This is explained by fast double bond shifts.



$$\mathrm{C{-}\underset{\substack{|\\C}}{C}{=}C + C \rightarrow C{-}\underset{\substack{|\\C}}{C}{-}C{=}C \rightleftarrows C{-}\underset{\substack{|\\C}}{C}{=}C{-}C \rightleftarrows C{=}\underset{\substack{|\\C}}{C}{-}C{-}C}$$

(iv) In the case of methylpropene incorporation a major increase in the yield of 2-methylpent-2-ene is found. To a minor extent this is also true for 4-methylpent-2-ene. This tendency is also very pronounced in the C_7 fraction as shown by the important increase for 2-methylhex-2-ene.

Chain propagation at the secondary carbon atom of 1-olefins also seems possible. Proof for this is found in the increase of 2-methylbut-1-ene and 2-methylbut-2-ene, which are interconverted by rapid double bond shift around a tertiary carbon atom. This route is possible only for addition of C_1 species. The expected products for addition of C_2 and C_3 species were not detectable (*28*).

In no case were quaternary carbon containing products found. This means that carbon attachment to the tertiary carbon atom in methylpropene is excluded.

DISCUSSION

Overview of the Facts to be Accounted for in a FT Mechanism

The observations made in the present

TABLE 3

Product Distribution over Ruthenium on Aerosil upon Incorporation of C_4 Olefins, in the C_5, C_6, C_7 Hydrocarbon Fractions as Percentage of the C_5, C_6, and C_7 Fraction, Respectively

Product	Blank experiment	1-Olefins added	
		Methylpropene	1-Butene
3-Methylbut-1-ene	1.1	1.3	1.0
2-Methylbutane	3.5	3.8	3.1
1-Pentene	39.6	37.0	38.0
Pentane	26.4	20.8	26.5
t-2-Pentene	15.6	7.2	14.8
c-2-Pentene	9.3	5.2	9.9
2-Methylbut-2-ene	3.3	19.8	5.3
2-Methylbut-1-ene	0.6	4.3	1.3
4-Methylpent-2-ene	0.6	6.4	0.2
2-Methylpentane	1.7	1.0	3.0
3-Methylpentane	27.5	21.4	27.5
1-Hexene	31.1	19.4	31.5
Hexane	8.2	1.5	7.2
t-Hex-2-ene	17.9	7.4	16.2
c-Hex-2-ene	1.7	2.2	2.4
2-Methylpent-2-ene	0.0	22.3	0.0
3-Hexene	1.4	5.6	11.2
Heptane	38.5	18.9	40.0
2-Heptenes	17.4	9.1	15.8
1-Hepten	18.9	0.0	17.4
2-Methylhex-2-ene	9.8	58.8	9.5
3-Heptenes	13.8	4.1	12.3

study stress how important the acido-basic properties of the catalyst support are in the Fischer–Tropsch synthesis. This seems to be well-known in industrial practice (*23*) but has never been considered in mechanistic speculations upon the reaction intermediates. The very pronounced influence of support acidity upon the hydrocarbon growth factors must somehow be accounted for in mechanistic proposals. In this respect, the following results of this work are important:

(i) On a clean metal surface methane and carbon dioxide are the initial products formed in a FT synthesis.

(ii) A gradual change of the catalyst to steady-state working conditions occurs, as shown by the gradual decrease of the CO_2 yield, the increase of chain length of the products, and the increasing yield of higher hydrocarbons.

(iii) The acidity of the catalyst support determines the time at which constant growth probability of the hydrocarbon chain is reached: the higher the acidity the longer the time required to reach steady state growth.

(iv) Added steam intensifies all the phenomena.

(v) The incorporation of 1-olefins into a growing chain is dependent upon the acidity of the support and the structure of the olefin.

Besides these phenomena, the following well-known observations, reported already in the literature, should be taken into consideration:

(vi) Carbon dioxide causes an increase in growth probability on nonbasic catalysts. This behavior is different on alkali oxide-promoted supports, which behave indifferently to CO_2 (*23*).

(vii) On Ru, Co and Fe, C–O–H bands were clearly seen by ir spectroscopy, while this was not the case for Ni (*24*).

(viii) Low conversion over less active or deactivated catalysts generally shows high methane selectivities.

(ix) Any proposed model which describes product selectivity fails to predict the CH_4 content. The methane yield is always higher than the theoretical expected amount. This is true for the so-called Schulz–Flory (*18*), or Anderson model (*29*) but also for the recently proposed more general Extended–Schulz–Flory model (*30*). This indicates that the growth probability which is fairly constant for C_2 hydrocarbons on the so-called classical catalysts (such as Co promoted on kieselguhr), is always substantially lower at C_1.

New Proposal for the Mechanism of FT Synthesis of Hydrocarbons

Any proposal to explain the chemical nature of reaction intermediates in a FT synthesis should be compatible with the abovementioned nine key observations.

Initiation

The phenomena occurring on a clean surface in the initial period of the reaction can be explained quantitatively by a carbon monoxide disproportionation reaction followed by hydrogenation to methane of the surface carbon (Eqs. (1)–(3)). Thus a carbide mechanism is definitely possible for methane formation. Analogous results on other catalysts are reported in the recent literature and support the carbide intermediate theory (*6, 12–14*).

Intermediate for Chain Propagation

In the recent literature (*6, 12–14*) the carbide mechanism was extrapolated to chain growth as well. However, it appears that chain propagation must be initiated by a surface species different from the carbidic one as results from the following remarks: (i) during carburization of the metal surface, no higher hydrocarbons are formed nor are they during the initial reaction period when a precarbided surface is used; and (ii) the carbide theory does not explain—the intermediates being partly hydrogenated or not—how parameters such as acidity of the catalyst support and steam concentration can have such a profound influence on chain growth.

It is clear that coaddition of steam (this work) and carbon dioxide (*23*) both have similar favorable effects on chain growth. It further seems that the duration of the initiation period is determined by the activity of the catalyst in the water–gas shift conversion. Indeed, it was found that the lower the acidity of Ru-loaded zeolites, the higher was the activity in the water–gas shift reaction (*30*):

$$H_2O + CO = CO_2 + H_2.$$

Therefore, depending upon its activity as shift catalyst, the FT catalysts transform the CO_2 formed by the Boudouard reaction into water at a different rate. The higher the basicity of the support, the faster will be the reverse shift reaction and water will be formed at an earlier stage of the reaction. Water in its turn helps to form a surface intermediate capable of initiating chain growth. It is straightforward to assume that the latter species is oxygen-containing.

It could be argued that competitive sorption of water could enhance the mobility of "sorbed CH_2 radicals" during the transient period of the reaction. However, in such a case a decreased growth factor α and the formation of shorter carbon chains would be expected. Our results indicate that the opposite is true. Furthermore, the existence of an insertion mechanism of "CH_2"-species into a metal-alkyl chain was ruled out on firm experimental grounds. Indeed, the existence of a particle size effect in FT is not consistent with such a reaction mechanism (*32*). Meanwhile, the existence of a particle size effect has been confirmed for totally different systems (*34*).

Incorporation of 1-olefins into a growing hydrocarbon chain seems to proceed much more rapidly on acidic surfaces. This indicates that chain propagation is enhanced by Brønsted acidity. Combining this observation with the behavior of water described above, it seems likely that an alcohol-like intermediate should be formed on the acid sites from these olefins before incorporation in the chain is possible. Under the present reaction conditions most probably oxonium ions are formed on the acid sites between olefins and water, which are then "spilled over" to the metallic sites on which incorporation occurs.

Kummer *et al.* (*26, 27*) found almost three decades ago that both primary and secondary alcohols could be incorporated into growing chains with a selectivity of incorporation similar to that in the present work. By radioactive tracing it was found that no degradation of the alcohol to carbenes had occurred. The later criticism upon this work (*3*) that alcohols were probably dehydrated under FT conditions is refuted by the present data. Indeed, if this criticism were valid, it would be expected that water (or carbon dioxide) has a negative effect on chain growth.

In view of this the difference in the incorporation of but-1-ene and isobutene can be understood. From but-1-ene both the secondary and the primary alcohol can be formed and as a result incorporated. With methylpropene only the primary alcohol can be incorporated. Incorporation of tertiary butanol seems not possible, since quaternary carbons are never found in the products. The favorable effect of added steam in the case of but-1-ene and the negative effect for isobutene can be understood in the same way.

Mechanism for Chain Propagation

The previous argument for chain propagation can be rationalized in terms of the following scheme:

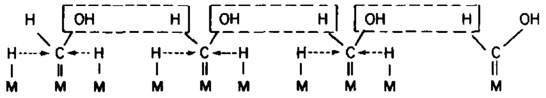
$$[C] + H_2O \rightleftarrows [CHOH] \quad (5)$$

$$2[CHOH] + H_2 \rightleftarrows [C_2H_4OH] + H_2O \quad (6)$$

$$[C_2H_4OH] + [CHOH] + H_2 \rightleftarrows [C_3H_6OH] + H_2O \quad (7)$$

and so on. The species in square brackets refer to intermediates chemisorbed on the FT active metal. Upon further dehydration these chemisorbed alcoholic intermediates can easily be desorbed as 1-olefins. Since it was reported that under a high growth probability, oxygenated species seem to be abundant on the surface (*6, 13*), it may be presumed that the dissociation of CO is a slow step in the succession of the events.

We reported earlier a metal particle size effect on FT activity and selectivity (*31, 33*). This can be understood if hydrocondensation of adsorbed C_1 units occurs as follows:



which gives 1-alcohols or 1-olefins as final products, depending upon the acidity of the support and the hydrogenation power of the metal. In such a scheme, the free migration of the growing alkyl chain is excluded. The intermolecular dehydration of the C_1 species should also be more rapid than the intramolecular dehydration of the chain or the subsequent desorption of 1-olefins as found earlier (*32*).

Hence a carbide mechanism is proposed for methane formation and a hydroxy-condensation mechanism for chain prolongation. The competition of surface carbides for hydrogenation or hydroxyl formation explains why the amount of methane formed cannot fit into any polymerization scheme. The higher the hydrogenation power of the metal, the more will direct hydrogenation be the preferred pathway. It results also that on a typical methanation catalyst such as nickel metal, no C–O–H bonds can be detected *spectroscopically*. Although on most nickel-based methanation catalysts also smaller amounts of hydrocarbons are formed (*35, 36*), it does not necessarily result that a different chain growth mechanism would be operative. Since the relative amount of water is a determining factor in the concentration of chemisorbed =CHOH species, it is also clear that at low CO conversion or on deactivated catalysts the relative amount of methane will increase in the products.

CONCLUSIONS

By a series of well-chosen experiments under conditions where high hydrocarbon growth rates occur, it is shown that polar conditions (acidic catalysts and addition of water) stimulate chain propagation in FT synthesis. While surface carbides are shown to be possible intermediates in methane formation, no evidence could be found that these intermediates are able to hydropolymerize to higher hydrocarbons.

The proposed mechanism includes therefore a disproportionation reaction of carbon monoxide which initiates the reaction and accounts for the initial CO_2 formation. The surface carbon is then hydrogenated to methane, while the reverse water–gas shift equilibrium accounts for water formation. Water with surface carbon forms hydroxy-species, which initiate chain propagation. Indeed, they undergo a condensation with water elimination and hydrogenation. Free motion of the alkyl chains is not possible and this explains the particle size effect in FT chemistry.

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