JOURNAL OF CATALYSIS 58, 95–107 (1979)

Incorporation of Surface Carbon into Hydrocarbons during Fischer–Tropsch Synthesis: Mechanistic Implications

P. BILOEN, J. N. HELLE, AND W. M. H. SACHTLER

Koninklijke/Shell-Laboratorium (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam-N, The Netherlands

Received September 18, 1978

To assess the role of carbidic intermediates in hydrocarbon synthesis we have studied the incorporation of surface carbon into hydrocarbon products. To this end, supported transition-metal catalysts (Ni, Co, and Ru) have been precovered with carbon, deposited via the Boudouard disproportionation of ^{13}CO. Subsequent exposure of these catalysts to ^{12}CO and H_2 led to the abundant production of $^{13}CH_4$ and of hydrocarbons containing *several* ^{13}C atoms within one molecule. From this we conclude that oxygen-free species CH_x ($x = 0$ to 3) are possible intermediates in methanation and that they are capable of being incorporated into growing hydrocarbon chains. Our results suggest that in the Fischer–Tropsch synthesis CO dissociates in a fast step to give carbidic intermediates, from which both methane and the higher hydrocarbons are produced.

I. INTRODUCTION

The oldest mechanism proposed for the "Fischer–Tropsch" process (*1*) assumed that a metal carbide is hydropolymerized to hydrocarbons. This concept was subsequently replaced (*2*a, b) by a hypothesis which distinguishes initiation, propagation, and termination steps and assumes that in each propagation event one carbon atom is added to the growing chain. The product distribution, which agrees with that calculated for Flory-Schulz polymerization kinetics (*2*c), gave strong support to the second concept, while the old carbide hypothesis fell into disgrace.

However, in the modern view, where the growing chain is linked to the catalyst surface by one terminal carbon atom only, the initiation "step" still consists of several elementary acts where a C–O bond is broken and several C–H and O–H bonds are formed, and the propagation "step," likewise, is the result of a reaction sequence including the formation of C–C and possibly C–H and O–H bonds while a C–O bond is broken. No evidence based on chain length distribution only can decide whether, in chain initiation, the C–H bond is formed prior or subsequent to the dissociation of the C–O bond, and for the propagation any sequence of C–O bond rupture and C–C bond formation is compatible with the Schulz–Flory product distribution. Distribution data of hydrocarbons, therefore, by no means preclude the possibility that in the initiation and/or the propagation event(s) the adsorption of CO is dissociative, an adsorption complex thus being formed, which might be called a "surface carbide."

Most authors (*2*b) have hitherto intuitively assumed that chain propagation

0021-9517/79/070095-13$02.00/0

on Fischer–Tropsch catalysts proceeds via "insertion" of a CO molecule between a surface metal atom and a carbon atom. This insertion is sometimes, more correctly, specified as the migration of an adsorbed alkyl group onto an adsorbed CO molecule. After this propagation step proper further hydrogenation is assumed to remove the oxygen atom from the carbon atom. This view is based on the analogy with concepts popular in the chemistry of metal carbonyls, and it provides an easy explanation for the formation of oxygenated by-products. Also for the chain initiation it was often assumed that the adsorbed C–O molecule is first partially hydrogenated to an enolic or aldehydic species, which then loses its oxygen atom upon further hydrogenation.

However, recently, Araki and Ponec (*3*) and Wentrcek *et al.* (*4*) presented evidence that at least in the case of *methanation* surface carbon is a probable intermediate; i.e., CO dissociation precedes C–H bond formation. This prompted us to reconsider the question of the participation of carbidic intermediates in the Fischer–Tropsch synthesis.

We reasoned that in order to be a possible intermediate, surface carbon should be sufficiently reactive; i.e., it should appear at a sufficiently high rate in hydrocarbons when a catalyst precovered with carbon is being exposed to H_2/CO at the temperatures and pressures appropriate for Fischer–Tropsch synthesis. Hence, we concentrated on measuring the rates of incorporation of surface carbon into hydrocarbons during Fischer–Tropsch synthesis.

In order to quantify the phrase "sufficiently reactive" and to highlight some of the key features of the prevailing experiments, we will follow one carbon atom on its reaction pathway, from the moment of its impact on the catalyst surface as a reactant CO molecule until the moment of its desorption, when it has been incorporated into the hydrocarbon product. During the reaction the carbon atom passes through various intermediates and requires a total of τ seconds for its conversion. Although these simplifications are not essential we will ignore for the moment the statistical distribution in quantities such as residence times of individual molecules and confine ourselves to a homogeneous surface that allows of only *one* reaction pathway which consists of a series of irreversible steps (Fig. 1). Then the steady-state rate of product formation, dN_p/dt, the total number of chemisorbed intermediates present in the steady-state, $\sum_i N_i$, and the conversion time τ will be related according to:

$$dN_p/dt = (1/\tau) \cdot \sum_i N_i. \qquad (1)$$

When we start with an intermediate C_i instead of the reactant CO, the total time needed for its conversion, τ_i, should be shorter than τ (Fig. 1). Actually,

$$\tau_i \leqslant \tau \qquad (2)$$

is the quantification of the phrase "sufficiently reactive." According to its definition in Fig. 1, τ_i can be measured by depositing a known number of labeled intermediate species, N_i, onto the surface and measuring the rate of labeled product formation:

$$dN_p/dt = (1/\tau_i)N_i. \qquad (3)$$

It should be noted that whereas $\sum_i N_i$ in Eq. (1) refers to a steady-state coverage, N_i in Eq. (3) refers to a non-steady-state experiment. Actually we can—at least

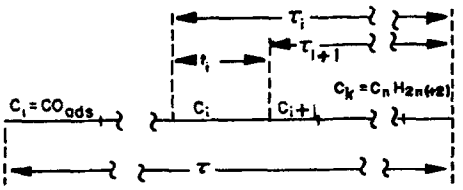


FIG. 1. Sequence of surface reactions. Carbon monoxide must reside on the surface for time τ in order to be converted to $C_nH_{2n(+2)}$. Any intermediate, i, needs τ_i with $\tau_i < \tau$. Note that $\tau_i - \tau_{i+1} = t_i$, the lifetime of species i.

"in principle"—determine the steady-state abundances of all the reaction intermediates by measuring τ_i, τ_{i+1}, etc., in separate non-steady-state experiments, because the residence time in state i, t_i, is given by (Fig. 1):

$$t_i = \tau_i - \tau_{i+1} \tag{4}$$

and the steady-state abundance N_j by:

$$N_j = (t_j/\tau) \sum_i N_i. \tag{5}$$

We have deliberately used the term "in principle," because in practice the pseudo-first-order rate constant $1/\tau_i$ in Eq. (3) depends on, for instance, the surface hydrogen coverage, which in turn depends on the coverage with other species. Ideally, one should therefore aim at depositing a small and known amount of labeled $^{13}C_i$ onto a surface which exhibits steady-state coverage of reaction intermediates from ^{12}CO, and determine $\tau_{^{13}CO}$ and $\tau_{^{13}C}$ simultaneously.

In our experiments the aforementioned considerations have been taken into account. A known amount of ^{13}C was deposited onto a known amount of surface-exposed metal atoms. Subsequently the system was exposed to $^{12}CO/H_2$ at a pressure ($\gtrsim 1$ bar) and temperature leading to synthesis of methane *and* higher hydrocarbons (cf. Section IIA on "Procedure").

While the actual experiment is only a rough approximation of the idealized experiment sketched above its results should be indicative of the participation of carbidic species in the Fischer–Tropsch synthesis. In the present paper quantitative data are presented for Ni and preliminary results for Co and Ru catalysts.

II. EXPERIMENTAL

A. Procedure. Approximately 2 g catalyst, exposing some 10^{20} metal atoms to the gas phase, is introduced into a small batch reactor. The total gas volume in the reactor, mainly porous volume and interparticle volume, amounts only to some 10 cm^3. Thus, although the Fischer–Tropsch synthesis is performed at $P \gtrsim 1$ bar, the total number of "C atoms in the gas phase" is not substantially larger than the number of surface-exposed metal atoms. This is a prerequisite because we have to determine product-from-(^{13}C)-surface carbon, present at fractional coverage (i.e., $N_{^{13}C} < N_{Me}$), and moreover have to limit the consumption of surface carbon to a *fraction* of what is present, in order to be able to apply Eq. (3).

Prior to the experiment N_{Me} is measured by *in-situ* hydrogen chemisorption, assuming a 1/1 ratio of adsorbed H to surface Ni or Co or Ru atoms.

Carbon is deposited by disproportionation of ^{13}CO at 250°C and an initial pressure of 0.5 bar:

$$2^{13}CO \rightarrow {}^{13}C_{ads} + {}^{13}CO_2,$$

and $N_{^{13}C}$ is determined by counting $^{13}CO_2$. Residual $^{13}CO_{ads}$ is removed from the surface by flushing with ^{12}CO.

The catalyst surface, covered with $^{13}C_{ads}$ and some $^{12}CO_{ads}$, is then exposed to $^{12}CO/H_2$, and the Fischer–Tropsch reaction is allowed to proceed until some 20% of all $^{13}C_{ads}$ has been consumed. The reaction gas is expanded into one of a series of containers, each with $V \gg V_{reactor}$, and the procedure is repeated. Thus, "one" experiment yields a series of product batches, synthesized over one and the same catalyst, which, however, has a decreasing $^{13}C_{ads}$ coverage. The batches are analyzed off-line with high-resolution mass spectrometry, allowing of the determination of the ^{13}C content of both methane *and* the higher hydrocarbons. The corresponding surface abundances in $^{13}C_{ads}$, $N_{^{13}C}$, follow from the initial coverage and the ^{13}C mass balance.

B. Materials. $Ni(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, and $RuCl_3 \cdot 3H_2O$ were the starting materials for our catalysts. The salts were deposited on SiO_2 (ex Kali-Chemie; pore

volume, 1.3 ml/g; mesh size, 30–80) from their aqueous solutions. Large batches of catalyst ($\approx$100 g) were dried at 120°C, and subsequently heated in hydrogen at a heating rate of 1°C/min, with a hold at 250°C and a final temperature around 500°C. After passivation they were stored under vacuum. Before use each reactor filling was subjected to an *in-situ* reduction at 450°C. Dispersions (number of surface metal atoms divided by total number of metal atoms), determined for each reactor filling separately via hydrogen chemisorption, proved to be fairly constant, running around 0.15, 0.02, and 0.06 for the 4 wt% Ni-, 15 wt% Co-, and 20 wt% Ru-SiO_2 catalysts, respectively. Dispersions were calculated from the total hydrogen uptake in 10 min at T = 0°C and P_{H_2} = 200 Torr (1 Torr = 133.3 N m^{-2}), assuming a stoichiometry H/Me = 1. For 4 wt% Ni/SiO_2 we verified that XRD line broadening [(200) reflection] yields the same value for the dispersion, within 10% rel.

^{13}CO with 93.6% ^{13}C was obtained in 100-ml stainless-steel bottles at 15 bar pressure from Merck, Sharp and Dome. Wherever appropriate we have accounted for the 6.4% ^{12}C-ex-^{13}CO in our mass balances.

C. Reactor hardware. The reactor hardware was mainly constructed from Hoke parts. The reactor itself, a U-tube, could be immersed into a (preheated) movable fluid-bed oven, thus allowing well-defined reaction times without the risk of overshoots in temperature.

The reactor as well as the calibrated containers from which it was being filled and into which it was being emptied were all equipped with calibrated pressure transducers. For each reactor filling the void volume in the reactor was determined by helium expansion. This set-up allowed *in-situ* hydrogen chemisorption and reconstruction of mass balances from the total pressures read, together with the compositions determined from mass analyses. It should be noted that the reactor effluent was removed by expansion into a vessel with a large (and known) volume rather than by pumping, in order to avoid removal of an unknown number of molecules.

D. Mass analysis. Mass analysis of the paraffins was performed on the parent peak at resolution (10% valley) $M/\Delta M \geqslant 10^4$, using a MAT-731 mass spectrometer.

Mass analysis is feasible because of (a) discrimination between ^{13}C and (^{12}C + H), resulting in C_nH_{2n+2} produced from $C_{n+1}H_{2(n+1)+2}$ via split off of $-CH_2$, being the only contaminant; and (b) a CH_2-split-off fraction of only some 10^{-2} at the excitation energy used (70 eV).

III. RESULTS

A. Reactions Involving CO Only

We measured the rate of CO disproportionation, the rate of exchange between gas-phase and adsorbed CO, and the rate of scrambling of oxygen atoms between adsorbed CO and carbon. Furthermore we verified via a mass balance that deposition of $^{13}C_{ads}$ via the CO disproportionation reaction leads to systems free of adsorbed ^{13}CO and/or dissolved oxygen. Finally we measured the extent of catalyst contamination by spurious carbon.

For the disproportionation or "Boudouard" reaction,

$$2CO_{gas} \rightarrow C_{ads} + CO_{2gas},$$

we measured initially, i.e., over the clean nickel surface, the following turnover numbers (molecules CO_2 produced per second per exposed Ni atom): 110°C, TON $\leqslant 2\cdot10^{-6}$; 170°C, TON = $9\cdot10^{-5}$; 250°C, TON = $2\cdot10^{-3}$. Note that these are turnover numbers measured in the *absence* of hydrogen, resulting from exposure to $\frac{1}{2}$ bar CO.

In order to find out whether $^{13}CO_{ads}$, whenever formed on the surface, could be detected in the gas phase we measured the

rate of the exchange reaction:

$$^{12}CO_{gas} + {}^{13}CO_{ads} \ (\rightleftarrows) \ {}^{12}CO_{ads} + {}^{13}CO_{gas}.$$

To this end we chemisorbed at 110°C 1.5×10^{19} molecules ^{13}CO onto 5×10^{19} Ni sites, and *subsequently* exposed this system for 300 s to 15×10^{19} molecules ^{12}CO. We then measured the following ratio in the gas phase:

$$^{13}CO/^{12}CO = 0.10 \pm 0.01.$$

The 10% imprecision is related to the type of residual gas analyzer used in this experiment rather than to an incompleteness of the exchange reaction. The *maximum* amount of nonexchangeable CO at 0.25 bar of CO at 110°C can then be calculated to be $\theta = 0.03$. We therefore conclude that any appreciable amount of ^{13}CO formed and/or present on the surface during the Fischer–Tropsch reaction (T = 170°C, Δt-batch = 10^2–10^3 s) in addition to ^{12}CO will be evidenced by the presence of $^{13}CO_{gas}$ in addition to $^{12}CO_{gas}$ in the reaction effluent.

As we attempt to determine the reactivity of C_{ads} in the presence of CO_{ads} via labeling, it is vital to verify that the rate of the oxygen scrambling reaction,

$$^{12}CO + {}^{13}C \rightarrow {}^{12}C + {}^{13}CO,$$

is insignificantly low. We measured the rate of this scrambling reaction in the *absence* of hydrogen by exposing 8×10^{19} ^{13}C atoms present on 10×10^{19} nickel atoms to 30×10^{19} ^{12}CO molecules for 300 s at 170°C. After exposure the CO_{gas} contained some 0.6% ^{13}CO only, pointing to a negligible surface concentration of ^{13}CO under these conditions. With regard to scrambling during the Fischer–Tropsch reaction, i.e., in the *presence* of hydrogen, we merely mention that for all the nickel results reported here the ^{13}CO content of the CO in the reaction effluent was measured and found to be well below 3%.

In order to verify that after the ^{13}CO disproportionation all the residual $^{13}CO_{ads}$

TABLE 1

Compilation of Turnover Numbers (TONs) for CH_4 Production over Ni[a]

Batch No.	Series 11			Series 15			Series 16			Series 20			Series 40	
	TON (10^{-4} s^{-1})	$\theta_{^{13}C}$[b]	$^{13}CH_4$ (%)	TON (10^{-4} s^{-1})	$\theta_{^{13}C}$	$^{13}CH_4$ (%)	TON (10^{-4} s^{-1})	$\theta_{^{13}C}$	$^{13}CH_4$ (%)	TON (10^{-4} s^{-1})	$\theta_{^{13}C}$	$^{13}CH_4$ (%)	TON (10^{-4} s^{-1})	
1	3.1	0.62	56	5.5	0.58	63	6.7	0.33	51	7.1	0.37	50	6.1	*Not*
2	4.5	0.50	58	3.3	0.39	38	—	0.21	30	3.3	0.20	25	3.3	precovered
3	4.5	0.41	37	2.9	0.28	22	4.1	0.14	17	2.4	0.13	14	1.6	with
4	2.9	0.32	24	2.4	0.21	16	3.4	0.11	13	1.8	0.08	11	1.2	$^{13}C_{ads}$
5	1.8	0.24	18				2.4	0.09	9	1.3	0.05	6	1.2	

[a] TONs calculated as molecules $^{12}CH_4 + {}^{13}CH_4$ produced per surface-exposed nickel atom per second. 4 wt% Ni-SiO_2; T = 170°C; P = 1 bar; H_2/CO molar ratio = 3. Note that TONs correlate with "time on-stream" rather than with $\theta_{^{13}C}$ (see Table 2).

[b] $\theta_{^{13}C} = N_{^{13}C}/N_{Ni}$ (cf. Fig. 3).

had indeed been removed by flushing with ^{12}CO, and that the nickel was free of dissolved oxygen, we counted in one case all the ^{13}CO, recovered by ^{12}CO flushing, and found:

$$\left[\frac{\frac{1}{2}\Delta^{13}CO - {}^{13}CO_2}{{}^{13}CO_2}\right] \leqslant 1.5\cdot10^{-2}, \quad (6)$$

in which $\Delta\ ^{13}CO$ is the net amount of ^{13}CO consumed during disproportionation.

In a separate experiment we determined to what extent the catalyst is contaminated with spurious ($^{12}C_{ads}$) carbon before it is subjected to $^{12}CO/H_2$. Thus, we subjected a supposedly clean reduced 4 wt% Ni/SiO_2 catalyst to an oxidation treatment with 1 bar O_2 at 500°C for 1 hr and analyzed for CO_2. The amount of CO_2 determined (50 Torr ml) corresponds to a θ (C on Ni) = 0.02, assuming all the carbon to be present on the nickel rather than on the support surface. Such a coverage with $^{12}C_{ads}$ is insignificant as compared with the ^{13}C coverages considered (being of the order of 0.5).

The rate of CO disproportionation over Ni/SiO_2, Co/SiO_2, and Ru/SiO_2 were found to be of the same order of magnitude.

B. Methanation and Fischer–Tropsch over Ni: Turnover Numbers, Product Distributions, and Isotopic Compositions

Turnover numbers for the production of methane over nickel at 170°C, 0.25 bar CO and 0.75 bar H_2 have been compiled in Table 1. It is worth noting that the TONs show a better correlation with the time on-stream than with the coverage with $^{13}C_{ads}$. Further, the initial TONs run around 6×10^{-4} (molecules CH_4 produced per Ni site per second), whereas the data suggest a steady-state value around 1.5×10^{-4}.

A typical example of a product distribution, represented as a Flory–Schulz plot [ln yield (%m) vs hydrocarbon chain length], is given in Fig. 2. The Flory–Schulz plot is close to linear with an α value (mol% C_{n+1}/mol% C_n) close to 0.33, with CH_4 almost on α level and with the undershoot of C_2 characteristic of Fischer–Tropsch product distributions. The amount of olefins in C_{3+} is close to 25 mol%.

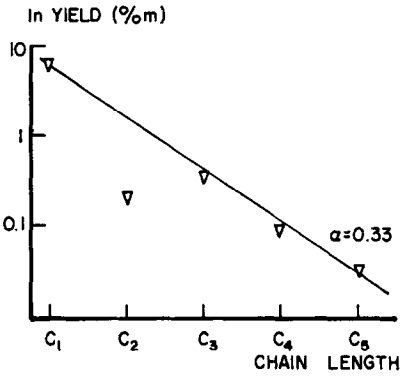


FIG. 2. Product distribution observed (▽) over Ni; ——, Flory–Schulz distribution for $\alpha = 0.33$. $T = 170$°C; $P = 1$ bar; $H_2/CO = 3$.

The isotopic composition of the CH_4 fraction has been plotted in Fig. 3. Note that $\theta_{^{13}C}$ has been *defined* as:

$$\theta_{^{13}C} \equiv N_{^{13}C}/2N_{H_2},$$

in which $N_{^{13}C}$ is the number of ^{13}C atoms deposited minus the number removed in prior batches as hydrocarbon product, and N_{H_2} is the number of H_2 molecules adsorbed at $T = 0$°C and $P_{H_2} = 100$ Torr. A detailed account of one series of batch experiments (series 20) is given in Table 2. Actually, as can be verified from Table 2, the θ values used in Fig. 3 have been calculated for each batch as the arithmetic mean of θ_{start} and θ_{end}. The results of batch experiments belonging to one series have been connected in Fig. 3 by lines. Note the abundant production of $^{13}CH_4$ from $^{13}C_{ads}$, which is easily observable despite the atmospheric pressure of the reactant gas ($^{12}CO + H_2$).

In Table 3 we give the isotopic composition of the higher hydrocarbons. Note the significant production of hydrocarbons containing *several* ^{13}C atoms in their

molecular skeleton, up to $^{12}C_1$ $^{13}C_3H_{10}$, which is perhaps the most significant finding of the present study. Note further that the atomic percentages of ^{13}C in methane and in the higher hydrocarbons are identical within the accuracy of the measurements (Table 4).

C. Preliminary Results for Co/SiO_2 and Ru/SiO_2

Compared to Ni/SiO_2 the Fischer–Tropsch products obtained over Co/SiO_2 and Ru/SiO_2 contain a much larger fraction of higher-molecular-weight producers, corresponding to Flory–Schulz parameters α of ≈ 0.7 and ≈ 0.8, respectively. The isotopic product distributions of the higher hydrocarbons, obtained at one $^{13}C_{ads}$ coverage only, are given in Table 5. It is worth noting that they display essentially the same feature as the product distribution over nickel, viz., significant production of hydrocarbons containing several ^{13}C atoms. There are two things worth noting, however:

(a) The isotopic product distributions have been obtained with a residual gas analyzer and not with high-resolution mass spectrometry. Thus, $M(^{13}C)$ and $M(^{12}CH)$ could not be distinguished; although this may have resulted in systematic errors in the quantitative analysis, it will not alter the conclusion with regard to the multiple occurrence of $^{13}C_{ads}$ within one molecule.

(b) With Ru we were unable to verify the absence of significant amounts of $^{13}CO_{ads}$ during the Fischer–Tropsch synthesis, because virtually all of the $^{12}CO_{gas}$ and $^{13}C_{ads}$ had already been consumed in the first run.

These results are thus of a preliminary nature.

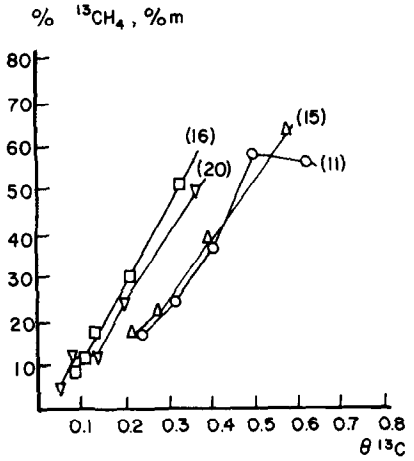


FIG. 3. Percentage of $^{13}CH_4$ in total CH_4 vs $\theta_{^{13}C}$. $\theta_{^{13}C}$ is defined as (number of ^{13}C atoms present)/(number of surface-exposed Ni atoms). The numbers in parentheses correspond to the serial numbers used in Table 1.

TABLE 2

Production of $^{13}CH_4$ with Varying $^{13}C_{ads}$ Abundance[a]

Series 20 batch	$^{13}C_{ads}$-start[b]	$^{13}C_{ads}$-end[b]	t (s)	$^{13}CH_4$[b]	$^{12}CH_4$[b]
1	59	29	480	21	20
2	29	18	660	6.5	20
3	18	12	720	3.0	18
4	12	6.7	960	2.2	18
5	6.7	4.3	1140	1.0	17

[a] ($^{13}C_{ads}$-start) − ($^{13}C_{ads}$-end) $\neq$ $^{13}CH_4$ because the balance of ^{13}C is present in the higher hydrocarbons. Number of surface-exposed Ni atoms = 120×10^{18}.

[b] Expressed in 10^{18} atoms (molecules).

IV. DISCUSSION

We will first draw what we consider to be the *minimum* conclusions. Next we will interpret the data in a somewhat imaginative manner and propose a detailed mechanism for "the" Fischer–Tropsch synthesis. We will attempt to demonstrate that this proposal explains our present findings in a natural way, and does *not* conflict with the most frequently quoted facts.

As to methanation, we observe an abundant production of $^{13}CH_4$ (Table 1, Fig. 3) under conditions where significant amounts of $^{13}CO_{ads}$ are absent (as attested to by a $\leqslant 3$ mol% ^{13}CO relative to ^{12}CO content in the reaction effluent, together with the proven rapid exchange between gaseous and

TABLE 3

Isotopic Composition of Methane and Higher Hydrocarbons[a]

Series	Batch	$\theta^{13}C$	CH_4		C_2H_6			C_3H_8[b]				C_4H_{10}				
			0[b]	1	0	1	2	0	1	2	3[b]	0	1	2	3	4
11	1	0.62	44[d]	56	45	46	9	16	30	37	17[c]					
	2	0.50	42	58	48	39	13	32	34	27	7					
	4	0.32	76	24	61	29	10	61	26	13	—					
	5	0.24	82	18	75	25	—	63	26	11	—					
5	1	0.36	38	62	49	30	21	31	27	28	14					
	2	0.27	54	46	51	30	19	55	26	14	6					
20	2	0.20	75	25	60	23	17	61	25	14	—	38	28	21	13	—
	3	0.13	86	14	78	22	—	73	21	6	—	48	26	24	—	—

[a] 4 wt% Ni/SiO_2; $T = 170°C$; $P = 1$ bar; H_2/CO molar ratio = 3.
[b] Number of all C_3H_8 molecules are $^{13}C_3H_8$ molecules.
[c] 17 mol% of ^{13}C atoms per molecule.
[d] Data given in mole percent.

adsorbed CO). This observation confirms the earlier conclusion of Araki and Ponec (*3*) and Wentrcek *et al.* (*4*) that there are reaction conditions under which carbidic carbon is a possible intermediate in methane formation. Because of the fact that the present data have been obtained at rather high pressures they can probably be extrapolated to "real" methanation, i.e. the production of substitute natural gas (SNG). When using $E_a = 110$ kJ/mol (*6*) our turnover numbers transform from 1×10^{-4} at 170°C into 30.5×10^{-3} at 275°C, which compares very well with the TONs reported for sulfur-free operation (*6*). We therefore conclude that *surface carbon, or any carbidic species CH_x which can be readily formed from it, is a possible intermediate in "the" synthesis of methane (SNG) from CO/H_2 over nickel.*

With regard to the synthesis of higher hydrocarbons we have clear-cut evidence of the abundant presence of molecules containing *several* ^{13}C atoms (Table 3). Therefore our minimum conclusion is that in nickel-catalyzed low-temperature hydrocarbon synthesis *a mechanism is operative that proceeds via insertion of carbidic species CH_x into growing hydrocarbon chains.*

In our opinion the present data suggest more than the conclusions formulated above. However, in order to draw additional "conclusions" we have to make rather drastic assumptions with respect to the usefulness of transient-state experiments, the nature of the carbidic carbon deposited, and the steady-state coverage of the catalyst with reactive intermediates.

The steady-state coverage of any ^{13}C species under ^{12}CO exposure being zero, the prevailing experiments are inherently of the transient-state type, and the validity of conclusions for steady-state operation is, of course, limited (cf. the trend in TONs of Table 1).

With regard to the coverage of our nickel catalysts with carbon originating from ^{13}CO disproportionation, we have no direct evidence to preclude a highly heterogeneous nature of the surface carbon such as might occur upon clustering at the surface or upon dissolution into the bulk. Merely on the strength of the low temperature at which the carbon deposition has been carried out, and in view of results reported

for deposition on a variety of well-defined nickel substrates (*7–9*) we assume that the carbon is present as a homogeneous submonolayer.

Using Eq. (3) we calculate the time needed to convert carbidic carbon into methane, τ^{13}_C. To this end we approximate N_i [Eq. (3)] by:

$$N_i = N^{13}_C \qquad (7)$$

in which N^{13}_C is the number of ^{13}C atoms deposited via the Boudouard reaction. In doing so we neglect labeled carbon blocked in unreactive positions or involved in chain growth rather than methane production.

From Eq. (1) we calculate τ^{12}_{CO}, the time needed to convert carbon monoxide into methane, approximating $\sum N_i$ [Eq. (1)] by:

$$\sum N_i = N_{Ni} - N^{13}_C \qquad (8)$$

in which N_{Ni} is the number of surface-exposed nickel atoms. The data in Table 6 can then be derived in a straightforward manner from Table 1, using the definitions for TON (dN_p/dt = TON·N_{Ni}) and for θ ($N^{13}_C = \theta_{13}\cdot N_{Ni}$). Table 6 shows two prominent features: (a) in each series of batches τ^{12}_{CO} and τ^{13}_C increase *simultaneously*; and (b) for each individual batch τ^{12}_{CO} and τ^{13}_C are about equal, an average over all the individual batches yielding:

$$\tau^{12}_{CO}/\tau^{13}_C = 1.0.$$

Note further that whereas the validity of $\tau^{12}_{CO} = \tau^{13}_C$ depends on the validity of Eq. (8), any substantial difference between τ^{12}_{CO} and τ^{13}_C would necessarily result in a *non*linear dependence of the percentage of $^{13}CH_4$ on θ^{13}_C, whereas Fig. 3 indicates a linear dependence.

From (a) we infer that a non-selective surface blocking process, rather than the disappearance or super-reactive carbon, underlies the trend of the TONs within each series (cf. Table 1).

On the strength of (b), $\tau_{COads} = \tau_{Cads}$, we propose that: (A) in the methanation reaction CO dissociates in a comparatively fast (and thus kinetically insignificant) step; and (B) "carbidic" species, CH_x with x = 0–3, constitute the most abundant *reactive* surface C_1 species [cf. Eq. (5)].

For the hydrocarbons synthesized over nickel we calculated the atomic percentages of ^{13}C, compared them to the % atomic percentages of ^{13}C in methane, and found the values to be equal within the accuracy of measurement (Table 4). We therefore propose that: (C) hydrocarbons and methane are formed from the same building blocks, i.e., oxygen-free species CH_x.

Proposals (A)–(C) lead to a picture in which the surfaces in our experiments are covered with a mixture of $^{13}CH_x$ and $^{12}CH_x$, in relative proportions determined by relations (7) and (8). When the intermediates from ^{12}CO and $^{13}C_{ads}$ are indeed indis-

TABLE 4

Comparison of the Abundance of ^{13}C in Methane With That in the Higher Hydrocarbons

Series 20 batch	Atomic percentages of ^{13}C in			
	CH_4	C_2H_6	C_3H_8	C_4H_{10}
2	25	28	18	25
3	14	11	11	19
4	11	10	4	6

TABLE 5

Isotopic Compositions; Preliminary Results Obtained with Co and Ru Catalysts

Series	Batch	θ^{13}_C	CH_4		C_3H_{18}			
			0	1	0	1	2	3
14[a]	1	0.9	27	73	62	26	10	2
	2	0.8	62	38				
	3	0.7	77	23				
30[b]	1	0.9	70	30	31	27	32	4

[a] 15 wt% Co/SiO_2; T = 170°C; P = 1.4 bar; H_2/CO molar ratio = 3; $\alpha \approx 0.7$.

[b] 20 wt% Ru/SiO_2; T = 170°C; P = 1.3 bar; H_2/CO molar ratio = 3; $\alpha \approx 0.9$.

TABLE 6

Time Constants, $\tau^{13}C$ and $\tau^{12}CO$, for the Converion of Carbidic Carbon and Carbon Monoxide into Methane[a]

Batch No.	Series 11		Series 15		Series 16		Series 20		Series 40[b]
	$\tau^{13}C$	$\tau^{12}CO$	$\tau^{13}C$	$\tau^{12}CO$	$\tau^{13}C$	$\tau^{12}CO$	$\tau^{13}C$	$\tau^{12}CO$	$\tau^{12}CO$
1	3.6	2.8	1.7	2.1	1.0	2.0	1.0	1.8	1.6
2	1.9	2.6	3.1	3.0	—	—	2.4	3.2	3.0
3	2.5	2.1	4.4	3.2	2.0	2.5	3.9	4.2	6.3
4	4.6	3.1	5.5	3.9	2.5	3.0	4.0	5.7	8.3
5	7.4	5.1			4.2	4.2	6.4	7.8	8.3

[a] See Discussion section. Units: 10^3 s.

[b] *Not* precovered with $^{13}C_{ads}$.

tinguishable, then their incorporation into growing chains would follow from elementary statistics; i.e., the probability of the synthesis of the hydrocarbon $^{13}C_i$ $^{12}C_j$ would equal the term $a_{ij}\theta_{13}{}^i\theta_{12}{}^j$ in the expansion of $(\theta_{13} + \theta_{12})^{i+j}$. In Fig. 4 we compare the observed and predicted distributions. Considering the ad hoc nature of assumption (8) and the difficulties associated with the mass spectroscopic analysis of the isotopic compositions, we regard the match as being satisfactory.

When comparing the present results and conclusions with relevant literature data, the following remarks appear appropriate:

[1] Kummer *et al.* (*10*) demonstrated that some metal carbides are *not* converted to hydrocarbons under ordinary reaction conditions. Likewise, Blyholder and Emmett (*11*) found that the CH_2 group of CH_2CO is *not* being converted into reactive intermediates, whereas the CO group *is*. Later studies disclosed other inactive carbides and other gaseous reactants which do not participate in chain growth (*2*). These studies contain circumstantial evidence, but in our opinion they fail to prove that CH_2 groups or surface carbon species, when present in the *appropriate* adsorption/coordination state at the surface, do not participate in the reaction. It may well be that in these studies the radioactive carbon merely ended up in an *inappropriate* state. For instance, Wise *et al.* recently observed that the surface carbon species formed from CO exhibit widely different reactivities in hydrogasification: Some carbon gasified at room temperature whereas graphitic carbon required gasification temperatures as high as 600°C (*12*).

[2] Della-Betta and Shelef recently performed *in situ* ir measurements during Fischer–Tropsch synthesis over Ru/SiO_2, and they observed the abundant presence of CO_{ads} (*13*). In addition, Barneveld and Ponec (*15*) recently presented evidence that the dissociation of CO_{ads} requires sites which are multiply coordinated ("Multisites") by suitable metal atoms. Therefore we propose that molecular CO is present on the "on-top" sites, showing up as a strong band in ir spectroscopy. As soon as a multisite becomes vacant it is in a rapid, i.e., kinetically insignificant, step filled with CO_{ads}, present already in the on-top positions. Thus, molecular CO_{ads} occupies the on-top positions and carbidic intermediates occupy the multisites.

[3] The rapid CO dissociation proposed in our model has to be reconciled with

our finding that the TON for CO disproportionation does *not* exceed the TON for methanation. Actually, similar observations have previously been cited as evidence *against* the carbidic theory (*2*). However, we would like to point out that our TONs for CO disproportionation have been measured in the *absence* of hydrogen. If these TONs are indeed sufficiently accurate (they have *not* been measured under differential conditions, i.e., at θ_{Cads} = const.), we have to conclude that under our conditions the CO dissociation is assisted by hydrogen. Interaction between coadsorbed CO and hydrogen has been observed repeatedly (*16*), and hydrogen-assisted CO dissociation has been reported recently (*17*).

[4] Della-Betta and Shelef recently showed that neither in methanation nor in the Fischer–Tropsch synthesis, both performed with a wide variety of transition metals, is any kinetic effect observed upon substitution of deuterium for hydrogen (*14*). Therefore they argued that in view of the unlikelihood

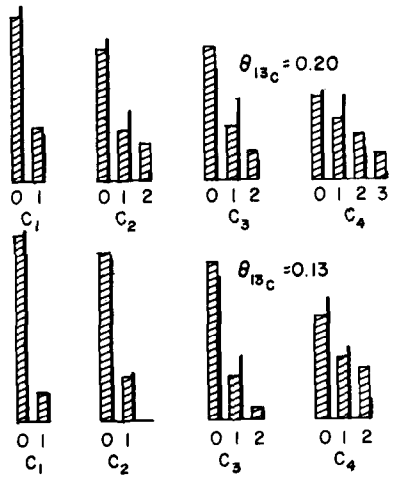


FIG. 4. Comparison of observed (▨) and calculated (|) abundances (series 20, batches 2 and 3). The abundance of $^{12}C_i$ $^{13}C_j$, P_{ij}, has been calculated as follows: $P_{ij} = (i+j)!/i!j!(1-\theta^{13}c)^i\theta^{13}c^j$.

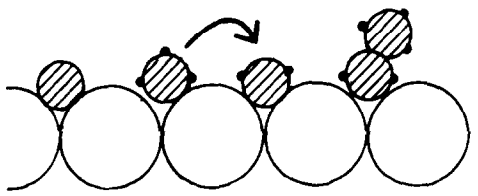


FIG. 5. CH_3-ads, ○ , jumps on top of CH_2-ads, ◎, to form CH_3CH_2-ads.

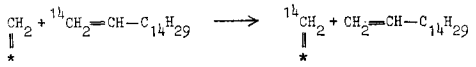
of hydrogen being involved in the rate-determining step, it is probably the CO dissociation that is rate determining. We would like to explain the absence of a primary hydrogen-isotope effect by postulating that a carbon-to-metal distance is the transition-state reaction coordinate featuring in "the" rate-determining step(s). This corresponds to reaction steps such as those depicted in Fig. 5, in which CH_3-ads jumps on top of CH_2-ads to form CH_3CH_2-ads. Further, by postulating that hydrogen competes with CO for the on-top sites our model accounts in the conventional manner for the overall kinetic features, including the variation of the Flory–Schulz parameter α with the H_2/CO ratio. With regard to the latter phenomenon, this may well explain the transient-state effects observed when removing CO from the feed. Removal of CO from the H_2–CO mixture may well result in a sudden increase in the coverage with H_{ads}, leading to the production of methane rather than higher hydrocarbons from the CH_x building blocks present.

[8] Thus, although at least one feature of our model for the Fischer–Tropsch reaction, i.e., the comparatively fast dissociation of CO_{ads} to give the monocarbon building blocks CH_x-ads, conflicts with most other proposals in the literature, we conclude that it can be defended in the light of the current literature. We would finally express as our opinion that if in due course the proposal that "CO dissociation is

relatively fast, i.e. kinetically insignificant," should prove to be false, then this is most likely to be due to Eqs. (7) and/or (8) giving a wrong estimate of the number of reactive surface species.

[5] As mentioned in the Introduction, a strong argument in favor of the insertion of *non*dissociated carbon monoxide is the formation of considerable quantities of primary alcohols and other oxygenated products with iron catalysts under certain conditions. The present data, which show that under different conditions dissociation of CO is essential, do not, of course, preclude the presence of a parallel reaction path. In particular we visualized that at high conversions and consequently high H_2O/H_2 ratios oxidic patches are formed on iron catalysts and that on those sites undissociated CO is inserted in adsorbed alkyl chains, resulting in alkoxy groups, which ultimately leave the surface of the catalyst as primary alcohols or aldehydes.

[6] Work by Pichler and Schulz (2a, 18, 19) with ^{14}C-labeled olefins has provided evidence that these molecules can be incorporated in growing chains. However, with $^{14}CH_2{=}CH{-}C_{14}H_{29}$ it was found that ^{14}C-labeled paraffins containing fewer than 16 carbon atoms are formed, and this result is ascribed by Schulz and Achtsnit (*20*) to a metathesis reaction taking place in addition to hydrocracking under Fischer–Tropsch conditions on a thoriated cobalt catalyst. Considering that metathesis has been demonstrated (*21*) to be a reaction involving surface carbenes CH_2 as essential intermediates, any evidence for metathesis is also evidence for the presence of surface carbenes. This result would be consistent with a reaction sequence where surface carbene reacts first with the labeled olefin:



as is common in metathesis, and subsequently the carbene is inserted in an alkyl chain:

This scheme of inserting carbene is one of the possibilities to rationalize the main result of the present paper that CH_x is inserted. Note the close similarity between this scheme and the single-site dehydrocyclization reaction proposed by Muller and Gault (*22*) for, e.g., the formation of methylcyclopentane from *n*-hexane over transition-metal catalysts:

In addition, Casey and Neumann (*23*) put forward the idea that carbenes are of importance in the chain-termination step of the Fischer–Tropsch synthesis. Thus it seems worthwhile to look further into the possibility of links existing between the catalysis of the Fischer–Tropsch, the metathesis, and the dehydrocyclization reactions, and to find out whether carbene intermediates are less rare than has been thought so far.

[7] During the completion of the present manuscript further evidence of the reactivity of surface carbon came to our knowledge. In two studies (*24*, *25*) it was observed that room-temperature hydrogenation of surface carbon produces hydrocarbons, demonstrating that a synthesis route via carbidic intermediates is possible. The present study goes one step further in that—by comparing the reactivities of C_{ads} and CO_{ads} during their *simul-*

taneous conversion—it indicates that the route via carbidic intermediates is not only possible but also probable. Actually, Rabo *et al.* (*24*) already suggested this approach in their concise discussion.

V. CONCLUSIONS

From the results presented in this paper we conclude that not only methanation and the initiation step in the production of larger hydrocarbons, but also their chain growth can take place on nickel catalysts via oxygen-free species CH_x, generated by dissociative chemisorption of CO followed by partial hydrogenation.

We further propose that in the presence of chemisorbed hydrogen the dissociation of CO is fast, i.e., kinetically not rate-determining, although it is somewhat slower in the absence of hydrogen. It takes, most probably, place on sites consisting of several metal atoms.

The reactive species CH_x might be a carbene or methylene CH_2 and in the steady state the multiatomic adsorption sites will be covered to a considerable extent by such species.

Nondissociatively adsorbed CO will be adsorbed on oxidized patches or in "on-top" positions where it competes with hydrogen adsorption. Its insertion might result in the formation of primary alcohols and other oxygenated species. For the formation of normal paraffins on Fischer–Tropsch catalysts, however, our results suggest that the predominant propagation is adequately described by:

$$C_mH_y + CH_x \rightarrow C_{m+1}H_{x+y},$$

where $x = 0$–3, probably with $x = 2$ and $y = 2m + 1$.

ACKNOWLEDGMENTS

The authors are indebted to Mrs. P. A. J. M. Hendriks and Keng Lim Huat for their skillful assistance, to Dr. A. L. C. Smit for supervising the mass analyses, and to Mr. E. Lesk (Merck, Sharp & Dome) for supplying ^{13}C-labeled-chemicals at high pressures in tailor-made containers.

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