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Cobalt–Thorium Catalysts for the Synthesis of Light Olefins from $CO–H_2$ Mixtures at Atmospheric Pressure in the Liquid Phase

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At 1 atm pressure, a new bimetallic system based on cobalt and thorium promotes the synthesis of principally light olefins from synthesis gas. The catalyst is prepared as a homogeneous solution and is further activated at 240°C by slurrying in a high boiling industrial solvent. A detailed analysis of the synthesized hydrocarbons is reported; the latter are mostly composed of linear α-olefins (>80% in the C_2–C_5 fraction) according to a Schulz–Flory distribution, except for C_2 hydrocarbons. The efficiency of the system has been investigated with regard to alterations of chemical parameters such as solvent, ligands, and deuterium. An inverse isotope effect was evidenced. The reactions and relative reactivities of some added molecules, namely, short-chain alcohols and α-olefins, are reported. Even under an inert atmosphere, olefin cracking and homologation occur to some extent. Ethanol and 2-propanol additions mostly yield C_1 species while 1-propanol addition yields C_2 species.

INTRODUCTION

Selectivity is a crucial problem in Fischer–Tropsch synthesis (*1–3*). It can conceivably be increased by catalyst modification. Basically, three approaches have been used in catalyst modification (*4*): shape-selective catalysts, polymetallic catalysts, and highly dispersed catalysts.

Those different strategies are not mutually exclusive. Moreover, CO reduction can be carried out either as a vapor phase or a liquid phase reaction. However, although liquid and vapor phase reactions may differ for many reasons, neither the properties of polymetallic particles dispersed in a liquid medium nor the consequences of generating particles in a fluid (effects on particle size, composition, etc.) have been much investigated.

Liquid phase oligomeric reduction of syngas at 1 atm pressure has been given only scant attention (*1, 2*). Interestingly, Blanchard and Petit (*5*) reported recently that Ziegler-type catalysts selectively reduced CO (from syngas) to light olefins. However, these reactions were hardly catalytic at atmospheric pressure. They were later shown to produce hydrocarbons and moderate amounts of oxygenates under pressure (*6*).

On the other hand, the important role of ThO_2 as a support (or catalyst?) is amply documented in heterogeneous catalysis, especially in the Fischer–Tropsch reaction. On the other hand, recent developments in the chemistry of the organoactinides has pointed out some unusual and particularly interesting properties of organoactinide complexes, notably the thermodynamically favored CO insertion into their metal–hydrogen bonds and ready coupling of the resulting "formyl" moieties (*7*).

The idea was to prepare *in situ* homogeneous mixtures of an actinide and a group VIII complex and to screen the properties of such mixtures for CO reduction.

The objective of this article is to report

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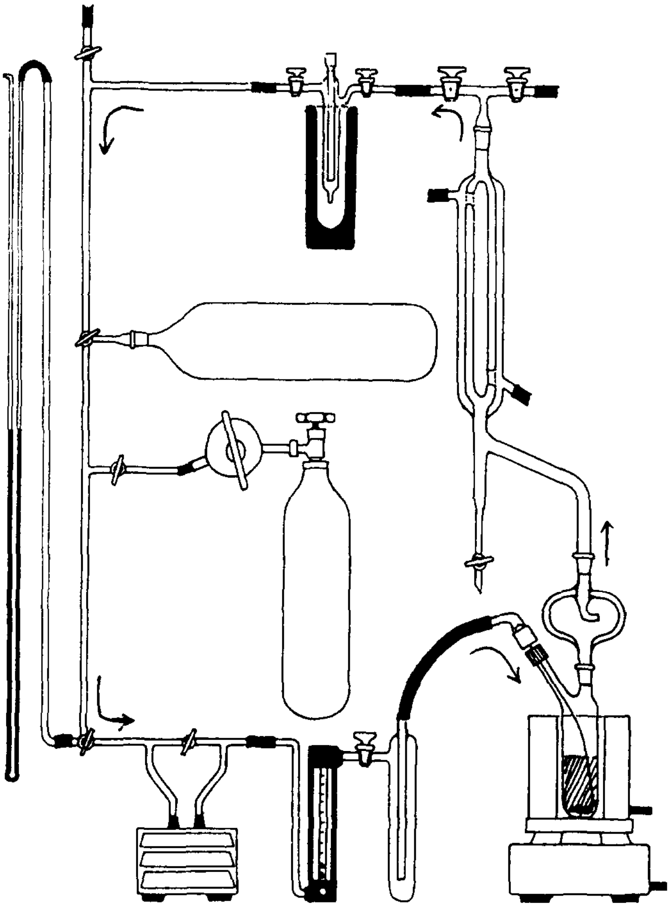

FIG. 1. Setup used for synthesis gas reactions at 0.1 MPa.

on the preparation and properties of a new catalyst based on soluble cobalt and thorium complexes after it has been slurried by heating in a high boiling, inert solvent. It is worthy of notice that such a homogeneously prepared catalyst is much more active (and selective for olefin synthesis) than the "corresponding" heterogeneous system prepared by impregnation of ThO_2 with cobalt carbonyl (thorium being used in amounts equivalent to or larger than those corresponding to the homogeneous case, all other parameters being held equal).

The catalyst promotes the formation of light hydrocarbons, mainly olefins, from synthesis gas at atmospheric pressure and with minimal side reactions. The reactions and effects of some added molecules (alcohols and olefins) on this particular system have also been examined.

EXPERIMENTAL

The catalyst is prepared by stirring (under an inert atmosphere) dicobalt octacarbonyl (5×10^{-4} mol) and thorium(IV) acetylacetonate (2.5×10^{-4} mol) in 40 ml of dry, redistilled Santotherm 66 until complete dissolution. Santotherm 66 is a high boiling (340–400°C) hydrogenated terphenyl from Monsanto which is principally used as a heat transfer fluid. The homogeneous red-brown solution is then slurried in the setup described in Fig. 1 by heating to the reaction temperature, usually

240°C, under a syngas atmosphere. This process takes about 1 h.

Synthesis gas (CO : H_2 = 0.5 in the standard conditions) is then continuously circulated through the catalyst suspension. The reaction products are retained in a cold trap refrigerated in liquid nitrogen. Unreacted syngas is recycled by means of a membrane pump with a flow rate of approximately 65 $cm^3\ min^{-1}$. The system is regularly supplied with fresh CO–H_2. The reaction is usually stopped after 5 h. The reaction products (gas and liquids) are then collected and carbon balance established by VPC using the internal standard method with the help of a Varian CDS 111 computer.

Some of the experiments (alcohol and olefin additions) were carried out in a single pass reactor, with no recycling of the feed gas. The reaction products were collected and analyzed as described for the full apparatus.

The homogeneous solution as such does not promote any catalytic reaction. It begins to decompose, around 190–200°C, to give black particles. Heterogenization is complete in about 2 h at 230°C. The particles are relatively homogeneous in size, 1–20 μm, as estimated by optical microscope examination. A light metallic mirror also appears on the vessel walls. It was checked by X-ray fluorescence that the mirror was exclusively made of cobalt while the particles contained both Co and Th. After filtration under an inert atmosphere (N_2), only the particles (when suspended in fresh solvent) were active for promoting the Fischer–Tropsch reaction.

The cobalt mirror as well as the filtered solution were inactive for promoting carbon monoxide reduction.

Isotope effect. The experiments were run with mixtures of CO–D_2 (ratios 0.5 and 1) instead of CO–H_2. Each experiment was done at least three times.

Olefin additions. Pulses of, respectively, ethene, propene, and 1-butene were added to the syngas, upstream of the reactor, at the steady state (20 pulses of 5 ml, i.e., 4.5×10^{-3} mol, one pulse every 10 min). The relative amounts of reaction products were then determined by VPC and the material balance of the hydrocarbon fractions made by comparing matched runs with and without added olefins.

Alcohol additions. Forty microliters of alcohols were added every half-hour to the reaction medium via the feed gas or under a helium atmosphere. Material balance was made as for the olefins.

Quantitative and qualitative VPC analysis were usually performed on three different columns: (a) H_2, O_2, N_2, CO, CH_4, and CO_2 on a Spherocarb column (Spherocarb GCA/012 from Analab Inc., 80–100 mesh, 1.5 m), with helium as carrier and a catharometer detector; (b) the light hydrocarbons (C_1–C_7) on a PLOT Al_2O_3–KCl fused silica column (50 m, 0.32 mm, Chrompack, ref 7515), N_2, FID; (c) the higher hydrocarbons (C_5–C_{15}) on a SE 30 column (2 m, 10% SE 30 on Chromosorb W, AW 45–60), N_2, FID.

RESULTS AND DISCUSSION

Catalyst Performance and Product Distribution

A real bimetallic synergy is observed, any of the two metals (Co or Th) used alone being practically inactive in our reaction conditions. Catalyst activity and selectivity are maximum for Co/Th ratios between 2 and 4.

Catalyst activity is 5 mol CO h^{-1} (mol Co)$^{-1}$ at the steady state. No appreciable catalyst deactivation is noticed after more than 40 h of reaction time.

The system proves to be selective for the synthesis of light hydrocarbons. The typical Schulz–Flory distribution (α = 0.47) in Fig. 2 shows the familiar pattern of a minimum at C_2 in the percentage plot (see below for a discussion of this particular effect). Up to 88% (molar basis) of the hydrocarbons are part of the C_1–C_5 fraction.

A detailed analysis of the isomer distribution of the synthesis products was carried

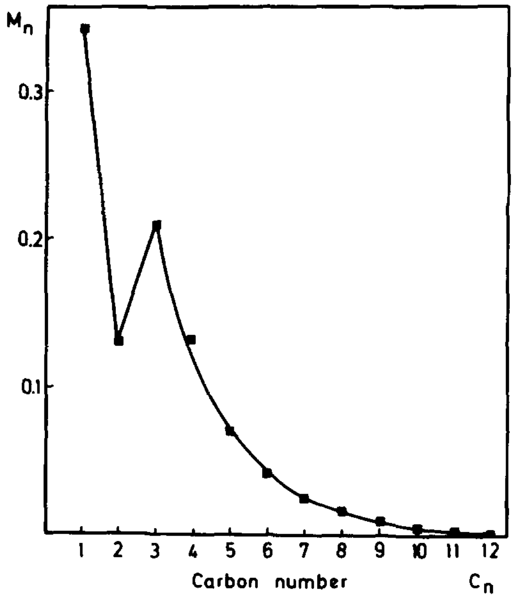

FIG. 2. C-number distribution for hydrocarbons, C_n (molar basis). Reaction conditions: 240°C, 0.1 MPa, $CO:H_2 = 0.5$.

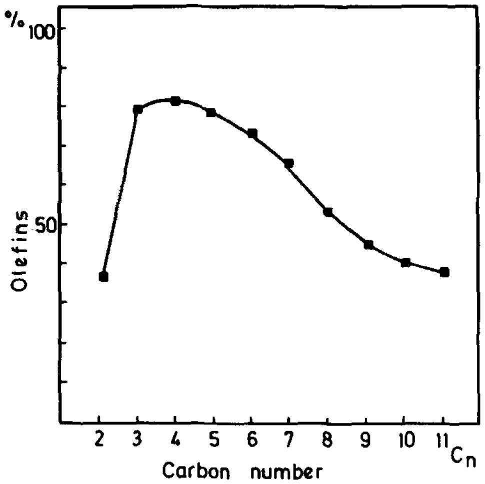

FIG. 3. Olefin content as a function of C-number, C_n.

out. The products are predominantly linear and Fig. 3 plots the olefin content as a function of the carbon number. Globally, unsaturation is higher than 70% (C_2–C_{11} fraction) and higher than 80% in the C_2–C_5 cut; 80% of the unsaturates are α-olefins. At high carbon number, the hydrocarbons are more saturated and contain more branching. Only monomethyl species were found in the nonlinear fraction. Figure 4 plots the variation of the ratio of normal to branched molecules with carbon number. Linear hydrocarbons are slightly more saturated than their isomers. This trend is exemplified in Table 1 for the C_4–C_6 fraction.

It is also apparent from Fig. 5, which plots the ratio of 1-olefins vs internal olefins as a function of C-number, that high-molecular-weight olefins contain more inner double bonds with a larger E to Z ratio (e.g., for 2-butenes and internal octenes, $E/Z = 1.2$ and 1.7, respectively): this is an indication that products evolve toward thermodynamic equilibrium at longer residence time. Indeed, increasing the syngas flow rate enhances the overall unsaturation and decreases isomerization: the shorter the residence time, the larger is the linear α-olefin fraction. However, the percentage of branched products does not vary significantly with contact time and remains practically constant throughout the reaction.

The above observations are in agreement with the now well-established proposition that α-olefins are primary products. They are also indicative that different sites could be responsible for chain growth and branching (*8*). Moreover, analysis of the reaction

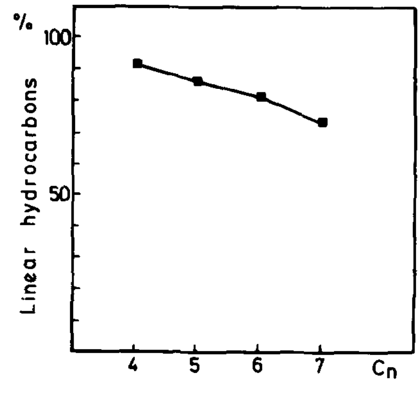

FIG. 4. Ratio of normal to branched molecules as a function of C-number.

TABLE 1

Olefin Content (wt%) of Linear and Branched C_4–C_6 Hydrocarbons

	Hydrocarbons		
	C_4	C_5	C_6
Linear	82	81	79
Branched	90	82[a]	81

[a] Composition of the total C_5 nonlinear fraction: 2-Me-butane 17%, 2-Me-1-butene 31%, 3-Me-1-butene 52%, 2-Me-2-butene traces.

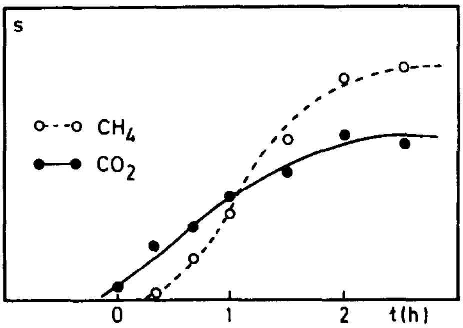

FIG. 6. Time dependence of CO_2 and CH_4 evolution.

products in the very early stages of reaction shows that CO_2 precedes CH_4 synthesis (see Fig. 6). This fact, however, is not a definite proof that CO dissociates to surface carbon initially if the water gas shift reaction is faster than CH_4 formation (*1*, *9*).

Effect of Temperature on Catalyst Activity and Selectivity

Reactions have been carried out at 200, 240 (standard conditions), and 275°C. Catalyst activity is low at 200°C. At 275°C, the overall activity is high but the mass distribution is strongly altered; $\alpha = 0.30$, which corresponds to a C_1 fraction ($CH_4 + CO_2$) of 80 vs 41% in the standard conditions (see Table 2). However, the relative amount of olefins in the C_2^+ fraction remains identical to that of the standard experiment run at 240°C. Hydrogenation and isomerization reactions of the higher hydrocarbons thus remain practically unchanged. Branching in the C_4^+ fraction is, however, somewhat higher at 275°C (see Table 2). The original catalyst activity is not entirely restored when the temperature is brought back to 240°C. It is then about two-thirds that of the standard conditions.

The C_1 fraction remains more important (62 vs 41%). However, the C_2^+ distribution pattern as well as the olefin content and branching are again very close to that of the standard conditions (see Table 2).

In fact, except for a higher methane production, chain propagation is similar to that initially observed at 240°C. Those facts are indicative that at least two independent reaction pathways take place: methanation

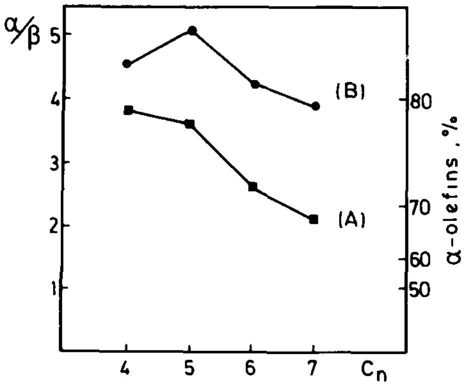

FIG. 5. Ratio of α- to internal (β)-olefins as a function of C-number: (A) CO : H_2 = 0.5; (B) CO : D_2 = 0.5.

TABLE 2

Variations of the C_1 Fraction and of Branching (wt%) as a Function of Temperature[a]

t (°C)	200	240-St	275	240-Bis
C_1	30	41	80	61.8
C_4-br	39	6.5	10	6.8
C_5-br	—	14.2	17.2	14.3

[a] Reaction conditions: 0.1 MPa; CO : H_2 = 0.5; temperature as indicated: 240-st = standard conditions; 240-Bis = 240°C after preliminary heating to 275°C; C_4-br and C_5-br refer to the relative amounts of the *non*linear isomers.

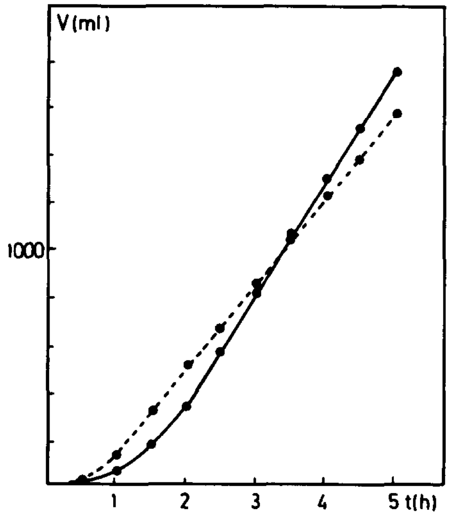

FIG. 7. Kinetics of CO reduction under deuterium or hydrogen. Full line, $CO:D_2 = 0.5$; dotted line, $CO:H_2 = 0.5$.

and chain propagation (methane synthesis included).

Thus it appears that sites responsible for propagation have been deactivated (possibly via a Boudouard reaction) or partially transformed into methane-producing sites. The above observations also support the suggestion of Sachtler *et al.* (*10*) that different sites are responsible for methanation and propagation, some sites being specific for methane synthesis. Moreover, we find here a further indication that sites responsible for chain-growth might be different from those responsible for branching.

Isotope Effect (IE)

A weak but significant inverse isotope effect is evidenced when the reaction is carried out with $CO–D_2$ ($CO:D_2 = 0.5$ and 1) in place of $CO–H_2$:

$CO:D_2 = 0.5,\quad k_H/k_D = 0.7–0.8,$
$\alpha = 0.54$
(cf. $\alpha = 0.47$ for $CO–H_2$)
$CO:D_2 = 1,\quad k_H/k_D = 0.8–0.9,$
$\alpha = 0.72$
(cf. $\alpha = 0.67$ for $CO–H_2$)

The IE is in direct ratio to the relative amount of deuterium. An example of the relative kinetics of CO reduction under hydrogen or deuterium is illustrated in Fig. 7. This latter graph also confirms what seems to be a general trend of the present catalyst system, i.e., a longer "induction time" when the reaction is carried out under deuterium. Chain propagation is then also favored (see α-values) and the olefin-to-alkane ratio increases, as summarized in Fig. 8. The higher olefin content goes with a lesser isomerization to internal olefins. The relative ratios of internal to α-olefins under $CO–D_2$ and $CO–H_2$ is given in Fig. 5.

Longer induction times, higher chain propagation, and lesser hydrogenation could be crudely accounted for by the higher dissociation energy of D_2 relative to H_2 (respectively, about 106 and 104 kcal mol^{-1}) so possibly there is less M–D available for chain transfer and termination.

However, the results available so far in the literature are contradictory: inverse, normal, or no IE have been reported for different systems. To investigate the chemical basis for these observations is very difficult due to the complexity and number of steps involved. The overall IE could arise from a combination of kinetic and thermodynamic effects, the former favoring the re-

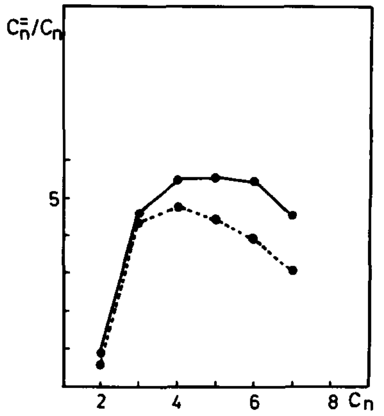

FIG. 8. Ratios of alkenes to alkanes synthesized under $CO:D_2$ (—) or $CO:H_2 = 0.5$ (···).

action of H_2 in the rate-determining step and the latter the reaction of D_2 (*11*). Nevertheless, the presence of an IE is probably indicative of one or several preequilibrium steps in the reaction mechanism (*12*).

Secondary Reaction of α-Olefins

The possibility of altering the molecular-weight distribution of Fischer–Tropsch products by addition of olefins to the synthesis gas has been considered (*13*).

Ethene, propene, and 1-butene were added separately to the catalyst at the steady state. The results of these experiments are summarized in Table 3 and compared to those in which the same olefins were added under hydrogen or helium in the single-pass reaction (no CO present).

Under CO–H_2 atmosphere. (a) The molecular-weight distribution is not markedly altered. The relative reactivities are ethene > propene ≫ 1-butene, this latter olefin being recovered practically unchanged.

(b) With ethene, hydrogenation to ethane and splitting to methane are the main reactions and account for about 80% of the added ethene. A significant fraction, however, is homologated to propene and 1-butene (respectively, 16 and 5% of reacted ethene).

(c) With propene the main reaction is homologation to butenes (12% of reacted propene), mainly 1-butene and isobutene. The amount of isobutene is anomalously high when compared to that of the standard conditions. Ethene and propene can thus participate in chain growth during CO hydrogenation. Olefin incorporation, however, is limited and seems correlated to the relative ability of the olefins to coordinate to the metal centers (ethene > propene). Propene incorporation yields linear as well as branched C_4 isomers.

Independently of the chain propagation reaction, the catalyst also promotes alkene hydrogenation. Hydrogenolysis of the hydrocarbons does occur, especially with ethene (or ethane).

TABLE 3

Reactions of Olefins; C-Number Distribution after Addition to the Catalyst[a]

	Hydrocarbons (wt%)				
	CH_4	C_2	C_3	C_4	C_5
	Under CO : H_2 = 0.5				
Ethene	19	70(63)	8.5(94)	3.5	—
Propene	3	5(88)	82(96)	6(96)	—
	Under H_2				
Ethene	31	57	8.5	3	0.5
Propene	25	5	67	2	1
1-Butene	8	1	4	85	2
	Under He				
Propene	1	1.5	96	1	0.5
1-Butene	1	traces	2	97	traces

[a] Reaction conditions: 240°C, 0.1 MPa. Numbers in parentheses refer to the olefin content.

(d) The active species are unaltered by the addition of olefins. Indeed, standard catalyst efficiency and selectivity are recovered shortly after pulsing. It was not possible, however, on the basis of gas consumption for short periods of time, to obtain an accurate measure of the variation of the steady state with the additive nor a measure of the rate at which it was re-established.

Under H_2 atmosphere. The reaction products are then mostly saturated hydrocarbons. However, some cracking and homologation also take place, in competition with hydrogenation, especially with ethene, by far the most labile olefin (see Table 3). A similar observation has been reported for a Fe-based catalyst (*14*). 1-Butene is essentially isomerized to 2-butene. Isobutane and isobutene are only present in trace amounts. A carbocationic type of mechanism is thus unlikely for explaining the presence of branched isomers.

Olefin transformations also occur under an inert atmosphere of He (see Table 3). The main reaction is then double-bond migration. For example, 1-butene is isomerized into 2-butenes. Again, very little isobutene is formed. Cracking or homologation into higher hydrocarbons is then extremely limited.

The above results indicate that the main secondary reactions of the primary α-olefins are hydrogenation and isomerization (double-bond migration).

The olefins may initiate chains or may become part of a growing chain only to a limited extent. With increasing carbon number, olefin incorporation, and cracking decrease, a probable consequence of the olefin relative ability to coordinate to a metal center. The incorporation of ethene does not lead to chain branching but that of propene does and propene incorporation may account at least for a part of the branched isomers. Ethene is by far the most labile olefin. This fact rationalizes the low ethene content in the product distribution.

Solvent and Ligand Effects

Carrying out the reaction in Santotherm 60 (S60), a nonhydrogenated polyterphenyl, instead of S66, brings about a large decrease in catalyst activity, although the α-olefin content is even higher. Although inert, S60 probably competes much more efficiently than S66 for active sites with CO and H_2. Solvent coordination not only reduces reaction rates but also affects the readsorption of primary products on the catalyst and hence the course of secondary reactions such as hydrogenation. Similar effects were reported by Satterfield and Stenger for a fused magnetite catalyst (*15*).

If aromatics, which are relatively weak ligands, promote such a drop of the turnover rate, it was expected that stronger ligands (e.g., triphenylphosphine, *N*-methylpyrrolidone) would severely depress hydrocarbon synthesis. This is indeed the case and the reaction is then completely stopped. A notable exception was oxygenated molecules: H_2O, acetone, alcohols. On an energetic basis, alcohols can be "incorporated" into the synthesis reaction to produce higher molecular weight hydrocarbons. To gain information on the mechanism of alcohol incorporation and in search of a possible support for oxygen-containing molecules as reaction intermediates, additions of methanol, ethanol, *n*-, and *i*-propyl alcohols were made to the catalyst system (see under Experimental).

Addition of methanol. The reaction $CH_3OH \leftrightharpoons 2H_2 + CO$, $\Delta G^\circ = -6.7$ kcal mol^{-1} at 240°C is thermodynamically favored. In fact, neither catalyst efficiency at the steady state nor product selectivity is affected when methanol is added to the standard system under syngas. Under He, methanol alone yields a hydrocarbon distribution very close to that observed under syngas, an observation also reported in Ref. (*16*) for a cobalt catalyst.

Addition of ethanol and propanols. Under a He atmosphere, the relative reactivities of ethanol and 2-propanol at 240°C are about the same, i.e., about 20% of conversion in the single-pass reactor. These two alcohols also yield the same overall distribution, namely, a mixture of hydrocarbons essentially composed of methane (see Table 4). On the other hand, 1-propanol is kinetically less labile under the same conditions and is essentially converted into C_2 hydrocarbons (>90% saturated). Those observations are indicative that C_2^+ alcohols react by pathways quite different from dehydration into the corresponding olefins, a thermodynamically disfavored reaction at 240°C (cf. Tables 3 and 4). Rather, those

TABLE 4

Reactions of Alcohols under Helium C-Number Distribution[a]

Added alcohol	Hydrocarbons (wt%)					
	C_1	C_2	C_3	C_4	C_5	C_4-Me
Ethanol	76	8(1)	10(43)	4(63)	2	13
2-Propanol	75	8(2)	10	6(28)	1	33
1-Propanol	22	56(8)	14	6(69)	2	11

[a] Reaction conditions: addition to the standard catalyst at 240°C, 0.1 MPa. Numbers in parentheses refer to the olefin content. C_4-Me refer to nonlinear isomers.

hydrocarbons seem to derive (at least formally) from the breaking of the C—C bond(s) which are α–β to the oxygen atom.

As far as the higher hydrocarbons are concerned, a further point of interest is that isopropanol yields a C_4 fraction which contains about three times as much of branched molecules than the two other normal alcohols. A related observation has been reported for a Fe–ThO_2 catalyst at atmospheric pressure (*17*). It has been proved by labeling experiments that more than 90% of the C_3 hydrocarbons resulting from labeled ethanol originated from the reaction of a surface methyl with the carbon of EtOH originally bearing the hydroxyl group. The same authors also noted the propensity of isopropanol to yield branched molecules (*18*), coupling therefore taking place at the central carbon.

These observations suggest that methanol (as expected), ethanol, and 2-propanol essentially generate C_1 surface species while 1-propanol favors the formation of C_2 species. Those species finally end up as mixtures of saturated (mostly) and unsaturated hydrocarbons, even in the absence of H_2. The real nature of the intermediates remains speculative, the presence of metal-alkoxy, -hydrocarbenes, or hydroxyalkyls as intermediates has been much discussed (*19*).

In conclusion, the observations reported in this study for a slurry phase Fischer–Tropsch catalyst are globally consistent with most of the previously established findings for related heterogeneous solid phase catalysts.

The narrower molecular-weight distribution as well as the high ratio of unsaturation can be (at least in part) rationalized by competitive adsorption effects as well as by the low pressure used. Moreover, strong indications that different sites could be responsible for chain-growth, methanation and, possibly, branching have been evidenced.

The nature and characteristics of the catalyst particles are presently under investigation. The results of those investigations will be presented in due course.

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