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Influence of Reaction Conditions on the Effect of Co-feeding Ethene in the Fischer-Tropsch Synthesis on a Fused-Iron Catalyst in the Liquid Phase

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ABSTRACT

The role of secondary reactions in the Fischer-Tropsch synthesis, particularly those involving ethene, has been revealed qualitatively in a number of studies. In this work, the kinetics of ethene hydrogenation and its contribution to synthesis reactions were quantified using a promoted fused-iron catalyst suspended in oil and contained in a stirred autoclave. The olefin-to-carbon monoxide pressure ratio in the reaction vessel was found to be the dominating factor with respect to both olefin selectivity during normal synthesis and the effect of added olefins. The widely varying results in the literature can be explained by a correlation with the actual olefin-to-carbon monoxide ratios and the carbon monoxide conversion levels applied.

INTRODUCTION

Addition of ethene to synthesis gas results in the incorporation of ethene, as found by many investigators for various types of catalysts, e.g., cobalt [1-6], ruthenium [7-11], rhodium [12] and iron [9,13-19]. Hydrogenation of ethene, however, is the most important reaction when ethene is added to carbon monoxide-hydrogen.

A small part of ethene added to carbon monoxide-hydrogen is hydrogenolysed to methane over cobalt catalysts [1]. The rate of hydrogenolysis increases with increasing temperature [4].

When ethene was added at levels similar to those produced by the Fischer-Tropsch synthesis itself, no olefin incorporation could be observed over Ru/Al₂O₃ according to Kellner and Bell [7]. At higher ethene concentrations, 0.5-1% incorporation (20-40 times that normally found in the reaction products) did occur over this catalyst but predominantly to C₃ and C₄. The formation of C₆₊ products was even suppressed.

In contrast to many cobalt catalysts, it has been reported for some ruthenium catalysts that addition of ethene causes a decrease of the methane production rate. Morris et al. [10] reported that methane production depends on the carrier. For magnesia and silica, methane formation was depressed whereas C_{3+} formation was enhanced. Silica or zeolite-supported ruthenium, in contrast showed an increase in methane production when 5 mol-% of ethene was co-fed.

Kim [9] reported a decrease in methane formation with ruthenium on titania on co-feeding 8.2 mol-% of ethene. In contrast, Morris et al. [10] and Kobori et al. [8] reported a decrease in methane production for silica-supported ruthenium when 20 mol-% of ethene was added. Despite this suppression of methane production, ethene was partly cracked into methane. Apparently, methane production from carbon monoxide is strongly inhibited by the presence of ethene. Recent work by Jordan and Bell [11] confirmed this conclusion. They found that methane formation with Ru/SiO_2 is inhibited by the presence of ethene in the feed. A tracer study showed that 90% of the methane formed was derived from ethene when 14 mol-% ethene was co-fed.

With iron catalysts, cracking of added ethene into methane can usually be neglected [3,13]. At extremely high temperature (743 K) added ethene is not only hydrogenated and incorporated but also cracked into methane [16].

Dwyer and Somorjai [15] demonstrated that a 1-alkene, produced as an initial product, can undergo readsorption in competition with carbon monoxide and hydrogen, and that such an alkene then contributes significantly to the synthesis of high-molecular-weight hydrocarbons. Addition of 0.04–2.7 mol-% ethene or propene to synthesis gas noticeably shifted the selectivity to heavier products.

The only work in the liquid phase was done by Satterfield et al. [17], who studied the addition of ethene and 1-butene in the Fischer–Tropsch synthesis on an iron catalyst. Less than 10% of the added amount of ethene (1.5 mol-%) seemed to disappear, apart from conversion to ethane. No noticeable effect of ethene addition on the olefin-to-paraffin ratio or the production of higher hydrocarbons was observed. Satterfield et al. concluded that addition of olefin to the reactant stream is not a viable method of altering the molecular-weight distribution over an iron catalyst.

Kim [9] claimed that methane production in the catalytic Fischer–Tropsch hydrocarbon synthesis reactions is reduced by adding olefins to the carbon monoxide–hydrogen feed mixture. α -Olefins with ten carbon atoms or less are particularly preferred. For example, with a precipitated iron catalyst 9.6 mol-% ethene was added to the synthesis gas and the carbon monoxide conversion remained unchanged whereas the methane selectivity was reduced by 30%. In a recent study, Snel and Espinoza [18,19] reported even a 50% reduction in the amount of methane formed with addition of 10 mol-% ethene over an iron–calcium catalyst.

The above studies resulted in a better understanding of the Fischer-Tropsch mechanism and the role of secondary reactions of olefins. The extents of the effects of co-feeding ethene (e.g., the percentage of added ethene converted to higher hydrocarbons) described in these studies differed widely and were probably strongly dependent on the reaction conditions. This dependence is described and explained in this paper.

EXPERIMENTAL

Synthesis gas either with or without added ethene was fed continuously into a 0.5-l, mechanically stirred autoclave about half filled with an essentially non-volatile and inert liquid, squalane ($C_{30}H_{62}$ = 2,6,10,15,19,23-hexamethyltetracosane) of >95% purity, in which the catalyst was suspended. The contents were stirred vigorously so the reactor behaved as a CSTR with respect to the gas phase, while mass-transfer resistances (G-L-S) were negligible. Thus the volatile products were continuously removed while the catalyst, inert liquid and a small amount of high boiling products remained in the reactor for the duration of a run.

The catalyst (from Süd-Chemie, designated C73) was a fused magnetite containing 2.0–3.0% Al_2O_3 , 0.5–0.8% K_2O , 0.7–1.2% CaO and <0.4% SiO_2 on an unreduced base. About 30 g of the crushed catalyst ($45 \mu m < d_p < 90 \mu m$) was prereduced in a separate vessel with hydrogen (900 ml/min) at $450^\circ C$ and atmospheric pressure for 72 h. Without air contact it was then slurried with the squalane to produce a 13 wt.-% suspension (unreduced base) and transferred to the reaction vessel. All measurements described were carried out at $250^\circ C$.

RESULTS AND DISCUSSION

Experiments without added alkanes

A large number of experiments were carried out at widely varying pressures, carbon monoxide-to-hydrogen ratios and conversion levels. Hydrogenation of olefins appeared to be the fastest and most important secondary reaction on the catalyst used.

The olefin selectivity can be described by a competition model of olefins and carbon monoxide. The model will be explained for C_3 . The concentrations of propene and propane depend on three reactions if secondary hydrogenation is considered as the only important consecutive reaction:

$$r_1 = k_1 C_{H_2,L} V_L \quad \text{propene formation from synthesis gas} \quad (1)$$

$$r_2 = k_2 C_{H_2,L} V_L \quad \text{propane formation from synthesis gas} \quad (2)$$

$$r_3 = k_3 C_{H_2,L} \theta_{C_3H_6} V_L \quad \text{secondary hydrogenation of propene to propane} \quad (3)$$

It is assumed that the formation of hydrocarbons from synthesis gas is first order in hydrogen for fused iron, in accordance with the finding of Huff and Satterfield [20] and results obtained in our laboratory [21]. The first-order hydrogen dependence is valid up to a conversion level of 70% for carbon monoxide-rich synthesis gas [20,21]. Südheimer and Gaube [22] determined the order in hydrogen, carbon monoxide and 1-alkenes for the formation of hydrocarbons and secondary reactions. They reported that all reactions involving hydrogen show a hydrogen order of nearly 1. The hydrogenation of 1-alkenes shows an order in 1-alkene also of nearly 1 [22]. Further, assuming that the hydrogenation of olefins occurs via the adsorbed olefin [23], eqn. (3) is obtained.

The C_3 olefin selectivity for an ideally mixed liquid phase reactor can therefore be expressed as follows:

$$\frac{p_{C_3H_6}}{p_{C_3H_6} + p_{C_3H_8}} = \frac{r_1}{r_1 + r_2} - \frac{r_3}{r_1 + r_2} \quad (4)$$

Replacing the hydrogen concentration in eqns. (1)–(3) by the hydrogen pressure, using Henry's law, and substitution into eqn. (4) leads to

$$\frac{p_{C_3H_6}}{p_{C_3H_6} + p_{C_3H_8}} = \frac{k_1}{k_1 + k_2} - \frac{k_3 K_{C_3H_6} p_{C_3H_6} / m_{C_3H_6}}{(k_1 + k_2) (1 + K_{CO} p_{CO} / m_{CO} + K_{H_2} p_{H_2} / m_{H_2} + K_p p_p / m_p)} \quad (5)$$

in which the fraction of propene on the catalyst surface ($\theta_{C_3H_6}$) is based on Langmuir–Hinselwood adsorption.

As CO is strongly bound on potassium-promoted iron [24,25], it will dominate the adsorption of hydrogen and of products at carbon monoxide conversion levels below 90%. Assuming further that the solubilities of propene and propane are approximately equal, eqn. (5) can be simplified to

$$C_3 \text{ olefin selectivity} = \frac{p_{C_3H_6}}{p_{C_3H_6} + p_{C_3H_8}} = A - B \cdot \frac{p_{C_3H_6}}{p_{CO}} \quad (6)$$

where $A = k_1 / (k_1 + k_2)$ and $B = k_3 K_{C_3H_6} m_{CO} / [(k_1 + k_2) K_{CO} m_{C_3H_6}]$. Note that the olefin selectivity does not depend on the hydrogen pressure in this model but only on the olefin-to-carbon monoxide partial pressure ratio.

With increasing carbon monoxide conversion, the ratio $p_{C_3H_6} / p_{CO}$ increases, implying a higher probability of olefins reaching the catalyst surface and being hydrogenated.

For carbon monoxide conversions below 90%, the validity of this model is demonstrated in Fig. 1.

On the catalyst used, propene is not cracked or converted to higher hydrocarbons and for this reason, the C_3 fraction gives a perfectly straight line. Eth-

Fig. 1. C_2 and C_3 olefin selectivity as a function of the $p_{C_2H_4}/p_{CO}$ and $p_{C_3H_6}/p_{CO}$ ratio, respectively, at a CO conversion level up to 98% (A, <90%, B, >90%). □, C_2 ; +, C_3 .

ene is capable of being incorporated into higher hydrocarbons, which causes the spreading in Fig. 1. Fig. 1 also demonstrates that neither the hydrogen partial pressure nor the total pressure is a suitable parameter for modelling the hydrogenation. It is demonstrated that at zero conversion ($p_{olefin}/p_{CO}=0$) the olefin selectivity does not approach 100%. At least some paraffins are initially produced.

Fig. 1 illustrates results covering the entire carbon monoxide conversion range, from 0 to 100%. Ethene is far more easily hydrogenated than propene. At carbon monoxide conversion levels higher than 90% the experiments no longer fit the model; the hydrogenation is inhibited. This phenomenon is caused by water and/or carbon dioxide molecules covering hydrogenation sites. This suggestion is based on experiments in which carbon dioxide was co-fed. These experiments show that the olefin selectivity increases with increasing pressure of carbon dioxide + water while the conversion level was kept constant (equal olefin-to-carbon monoxide ratio) [21].

The incorporation of ethene (the only alkene capable of being significantly incorporated) is illustrated in Fig. 2. This reaction causes the product ratio $p_{C_2}/p_{C_3-C_4}$ to decrease: the higher the carbon monoxide conversion (the higher the value of $p_{C_2H_4}/p_{CO}$), the more ethene is converted into higher hydrocarbons.

Ethene incorporation is thus responsible for deviations from Schulz-Flory

Fig. 2. $p_{C_2}/p_{C_3+C_1}$ Ratio as a function of CO conversion. Constant chain growth probability (α).

statistics at higher carbon monoxide conversion. At a low carbon monoxide conversion the Schulz-Flory graph is a straight line, without deviation of the C_1 and C_2 fractions. At higher carbon monoxide conversion ethene is converted into higher hydrocarbons, resulting in a lower C_2 concentration and a higher C_{3+} concentration. This concentration effect also causes the C_1 fraction (methane + ethanol) to deviate from the Schulz-Flory curve. However, this is not the only reason: ethene has an inhibiting effect on the methanation rate because H^* is scavenged from the catalyst surface for hydrogenation [11,19]. In addition, C_1^* may be scavenged from the surface by incorporation of ethene, which may be interpreted as a competitive reaction for the hydrogenation of C_1^* into methane. This suggestion is supported by the finding that the methane inhibition is proportional to the incorporation of ethene. The lower availability of surface hydrogen may play a minor role because it is expected that a strong decrease in H^* would lower the carbon monoxide conversion, which was not the case.

Cracking of ethene is an unimportant reaction on our catalyst under the reaction conditions applied, as proved by ethene hydrogenation experiments [26].

Isomerization of α -olefins to β -olefins increases with increasing carbon monoxide conversion. These results are not important with respect to this paper and are published elsewhere [21].

Addition of ethene

Four series of the experiments were carried out to investigate the effect of co-feeding ethene with the synthesis gas. A series consists of three experiments: the state before, during and after the addition of ethene. The reaction conditions applied are listed in Table 1. Material balances for the C_2 fraction, made by comparing matched experiments with and without added ethene, are listed in Table 2.

Series A

The results of this series of experiments are shown in Fig. 3–5. Ethene addition causes increased olefin selectivity, increased production of C_{3+} hydro-

TABLE 1

Addition experiments and reaction conditions applied

Series	Expt. No.	P (bar)	T ($^{\circ}C$)	F_{H_2} (ml/min)	F_{CO} (ml/min)	$F_{C_2H_4}$ (ml/min)	CO conversion (%)
A	1	9	250	40	61	0	70
	2	9	250	40	61	6.5	70
	3	9	250	40	61	0	70
B	4	1.5	250	40	61	0	15
	5	1.5	250	40	61	6.5	15
	6	1.5	250	40	61	0	15
C	7	1.5	250	73	25	0	25
	8	1.5	250	74	24	6.5	25
	9	1.5	250	73	23	0	25
D	10	9	250	104	150	0	55
	11	9	250	101	147	6.1	55
	12	9	250	101	145	0	55

TABLE 2

Material balances of added ethene

Parameter	Series A		Series B		Series C		Series D	
	$\mu\text{mol C/s}$	mol-%	$\mu\text{mol C/s}$	mol-%	$\mu\text{mol C/s}$	mol-%	$\mu\text{mol C/s}$	mol-%
Added ethene	9.043	100.0	9.043	100.0	9.043	100.0	8.487	100.0
Unconverted	3.407	37.7	8.774	97.0	7.072	78.2	7.204	85.6
Hydrogenated	4.053	44.8	0.219	2.4	1.560	17.3	1.189	14.0
Incorporated	1.583	17.5	0.050	0.6	0.411	4.5	0.034	0.4

Fig. 3. Influence of the addition of ethene on the methane selectivity. □, C_1 (bar)/ C_3 (bar); +, C_1 (bar)/ C_3 - C_5 (bar).

Fig. 4. Influence of the addition of ethene on the production rates of hydrocarbons. □, C_3 - C_5 ; +, C_1 + C_3 - C_5 ; Δ, C_1 + C_3 - C_4 .

Fig. 5. Influence of the addition of ethene on the olefin selectivity. +, C₃; ◇, C₄.

TABLE 3

Feeding ethene: changes in catalytic behaviour

Series	Expt. No.	Ol.sel. C ₃ ^a (%)	$r_{C_3-C_5}$ (μg/s)	C ₁ /C ₃	CO conversion (%) ^b	$p_{C_2H_4}/p_{CO}$
A	1	85	47	1.7	74	0.024
	2	87	54	1.4	73	0.190
	3	86	47	1.8	72	0.021
B	4	93	5	3	15	0.002
	5	94	7, 4.5 ^c	2.5, 3 ^d	15	0.118
	6	93	4.5	3.5	15	0.002
C	7	90	8.5	5.2	25	0.008
	8	90.5	12	3	25	0.293
	9	90	8	5.2	25	0.010
D	10	88.5	60	1.3	55	0.012
	11	88.7	60	1.2	55	0.080
	13	88.5	60	1.3	55	0.012

^aOl.sel.C₃ = $p_{C_3H_6} / (p_{C_3H_6} + p_{C_3H_8}) \cdot 100\%$.

^bCO conversion = $(CO_{in} - CO_{out}) / CO_{in} \cdot 100\%$.

^cDuring experiment 5 the production of C₃-C₅ hydrocarbons decreased from 7 to 4.5 μg/s (deactivation).

^dDuring experiment 5 the C₁/C₃ ratio increased from 2.5 to 3.

carbons and decreased methane selectivity. All these changes in catalytic behaviour are reversible and are presented in Table 3. Table 2 illustrates that the major part of the converted ethene is hydrogenated to ethane. The competitive adsorption of ethene reduces the availability of carbon monoxide surface intermediates. This is demonstrated by a decrease in the ethanol production, which is too large to be attributed to the reduction of C_1 surface intermediates. Remarkably, the carbon monoxide conversion itself is not affected by the addition of ethene although the availability of carbon monoxide surface intermediates decreases. Essentially this means that there is competition between the adsorption of ethene and a particular form of adsorbed carbon monoxide, which is involved in alcohol formation. It should finally be noted that there was no change in the chain growth probability.

Series B, C and D

The results of these series are qualitatively the same as those of series A, except the magnitude of the resulting effects is different. The results are presented in Tables 2 and 3.

The increase in the C_{3+} activity is caused by the incorporation of ethene. This reaction consumes a large amount of C_1 surface intermediates and therefore retards the methanation rate. The hydrogenation of ethene consumes H surface intermediates, which may have an inhibiting effect on both the methanation reaction and the hydrogenation of C_{2+} olefins.

In summary:

1. The increase in the C_{3+} activity is caused by the incorporation of ethene.
2. The decrease in the methane selectivity is caused mainly by a lower availability of C_1 surface intermediates and a higher concentration of C_{2+} hydrocarbons. The lower availability of surface hydrogen may play a minor role.
3. The increase in the C_{3+} olefin selectivity is caused by an enhanced adsorption of the very reactive ethene species. Also in this instance the lower availability of hydrogen may play a minor role.

Tables 1–3 illustrate the strong influence of the reaction conditions on the effects of co-feeding ethene. The effects are dependent on (i) the amount of ethene capable of reaching the catalyst surface, the $p_{C_2H_4}/p_{CO}$ ratio being the essential parameter to describe this adsorption competition, and (ii) the amount of ethene converted, which depends on the "activity" under the reaction conditions applied and can be expressed by the carbon monoxide conversion rate ($\mu\text{mol CO/s}$).

This means that the relative magnitude of the effects [e.g., decrease of methane selectivity (%)] is dependent on the $p_{C_2H_4}/p_{CO}$ ratio, whereas the absolute magnitude of the effects [e.g., decrease in methanation rate ($\mu\text{g/s}$) or increase in C_{3+} production rate ($\mu\text{g/s}$)] is dependent on the conversion level. Table 3 illustrates the correctness of this statement. It can be seen that the largest

Fig. 6. Amount of ethene added which is hydrogenated and incorporated as a function of $p_{C_2H_4}/p_{CO}$ ratio in the reactor, $\square$, $(r_{hydrog.} + r_{insert}) / -r_{CO}$; $+$, $r_{hydrog.} / -r_{CO}$; $\diamond$, $r_{insert} / -r_{CO}$.

decrease in the methane fraction, expressed by the C_1/C_3 ratio, is attained for the series with the highest $p_{C_2H_4}/p_{CO}$ ratio (C), whereas the largest increase in the C_3 – C_5 production rate is attained in series A in which the carbon monoxide conversion rate is much higher than that of series C.

Hence, finally, the amount of added ethene that is hydrogenated and incorporated over a fused-iron catalyst can be correlated with the $p_{C_2H_4}/p_{CO}$ ratio in the reactor, provided that the proportionality of this amount with the carbon monoxide conversion rate is accounted for, as shown in Fig. 6.

CONCLUSIONS

The principle conclusion is that the relative magnitude of the effects caused by adding ethene to the reactant stream is determined by the value of the parameter $p_{C_2H_4}/p_{CO}$ alone. This parameter is related to the carbon monoxide conversion and represents the reaction conditions applied (pressure, temperature, mol-% ethene added, etc.). The effects caused by co-feeding ethene agree completely with the effects of secondary reactions of ethene under normal Fischer–Tropsch conditions.

Although there is more or less complete consensus about the qualitative effects of adding ethene, our study explains why some investigators reported smaller effect than others (or even none).

Incorporation of ethene over iron catalysts has been reported by various groups [3,13,15,16,19], who also showed that the principal reaction of the added ethene was hydrogenation to ethane. Satterfield et al. [17], however, did not find any significant incorporation of added ethene or other effects. This conclusion was based on experiments with addition of ethene at too high a degree of conversion of carbon monoxide ($> 90\%$), with which all rates of reactions, including consecutive reactions, are reduced. Moreover, under these conditions it is very difficult to distinguish the reactions of a very small amount of added ethene.

A decrease in methane selectivity has been reported [9,15,19]. Barrault and Forguy [16], however, found an enhanced methanation rate, which was completely due to cracking of ethene on the iron/alumina catalyst at the extreme temperature of 745 K. As shown by all the other investigations, hydrocracking plays a negligible role on iron catalysts under normal Fischer-Tropsch conditions.

An increase in olefin selectivity has only been reported by Snel and Espinoza [19]. It is important to note that their reported effects of co-feeding ethene exceed all the former reported effects. This is due to the very high $p_{C_2H_4}/p_{CO}$ ratio, caused by adding a large amount of ethene under special conditions.

From a commercial point of view, the addition of olefins in the Fischer-Tropsch synthesis is only of interest for suppressing the methane production. One should realize that adding olefins strongly decreases the actual olefin production rate.

SYMBOLS

$C_{i,L}$	Concentration of component i in the liquid phase	mol/m ³
F_i	Gas flow of component i at atmospheric pressure and 20°C	ml/min
k_i	Reaction rate constant	1/s
K_i	Adsorption coefficient of component i	—
m	Solubility coefficient	m_G^3/m_L^3
p_i	Pressure of component i	bar
r	Rate	mol/s
T	Temperature	°C
V_L	Volume of the liquid	m_L^3
$\theta_{C_2H_4}$	Fraction of ethene on the catalyst surface	—
*	Surface intermediate	—

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