

Andreas Reul^{1,*}
Johannes Thiessen¹
Andreas Jess¹
Judith Scholz²
Angela Heykamp²


Co-Feeding of Ethene, Propene, and 1-Butene to Co-Mn-Catalyzed Fischer-Tropsch Synthesis

In Fischer-Tropsch synthesis (FTS), a variety of hydrocarbons with different chain lengths are formed. The selectivities depend on the catalyst and the reaction conditions. Co-feeding olefins allows changing the selectivity even outside the rules of the Anderson-Schulz-Flory distribution. In this work, ethene, propene, and 1-butene were co-fed to Co-Mn-catalyzed FTS to increase the olefin selectivity in the C₃- to C₈-fraction. An increase of the CO reaction rate and oxygenate selectivity indicates that besides FTS also hydroformylation takes place. While the predominant reaction is the unwanted hydrogenation of the co-fed olefins, this could in case of ethene be reduced by lowering the H₂ pressure.

Keywords: Fischer-Tropsch synthesis, Heterogeneous hydroformylation, Olefin co-feeding

Received: September 24, 2021; *revised:* October 29, 2021; *accepted:* December 01, 2021

DOI: 10.1002/ceat.202100488

 This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



Supporting Information
available online

1 Introduction

Fluctuations in the natural gas liquids and oil market, among other reasons caused by fracking, have favored light-end feedstocks for ethene production. Thus, steam crackers more and more run with ethane-only feed, and feedstocks such as naphtha became unattractive, resulting in a decline of C₃- and C₄-olefin production. Hence, the need for additional sources and routes for light and intermediate olefins for subsequent petrochemical processes has been arising. One option is conversion of syngas (H₂/CO) by Fischer-Tropsch synthesis (FTS) to hydrocarbons (alkanes, alkenes) and to a certain extent also to aldehydes and alcohols [1, 2]. Hence, FTS provides opportunities for a changing raw material landscape, as syngas can be produced from natural gas, coal, biomass or in future even based on renewable H₂ and CO₂ [3].

There are mainly two reasons for addition of alkenes to the syngas for FTS: for mechanistic kinetic studies of FTS, alkenes – typically ethene and propene – are often added in low concentration [4] and also C¹⁴-tagged [5], but studies with a partial pressure of ethene and propene of up to several bar were also conducted [6–9]. The effect of co-feeding alkenes to enhance the yield of products such as (higher) olefins and oxo-products has also been long considered. Already in 1938, Roelen realized in the context of investigations on FTS for fuels that C₃-oxo-products were formed by reaction of ethene with syngas [10]. This discovery has finally led to the development of the hydroformylation process, also referred to as oxosynthesis, today mainly with propene as feedstock and homogeneously catalyzed by Rh or Co complexes [11].

In a previous work, we have studied the influence of addition of Mn to a Co-based FT catalyst on the yield of olefins and oxo-products, but without co-feeding of olefins [12, 13]. The

best result, i.e., the highest olefin selectivity of about 50 %, was obtained for a Mn-to-Co mass ratio of 0.15. In this work, this catalyst now was used to investigate also the influence of co-feeding of ethene, propene, and butene on the reaction rates of CO, H₂, and each olefin as well as on the product distribution at various conditions (ratio of H₂/CO and olefin/CO, temperature). The focus hereby is on elongation of the co-fed species to C₃- to C₅-olefins as well as conversion to oxo-products which has not been studied in this detail before. Also trying to increase the olefin yield of an already olefin-optimized FTS Co-Mn-catalyst in this way is a novelty in FTS research.

2 Experimental

2.1 Reactor Setup and Experimental Procedure

The experimental setup is presented in Fig. 1. The fixed-bed steel reactor has an inner diameter of 1.4 cm and an isothermal zone of 25 cm. Subtracting the volume of the thermocouple guide tube the volume of the isothermal zone is 37 cm³; the volume of the catalyst bed is 25 cm³. The reactor is surrounded by an aluminum block (diameter 12 cm) to ensure isothermal

¹Andreas Reul, Dr.-Ing. Johannes Thiessen, Prof. Dr.-Ing. Andreas Jess
andreas.reul@uni-bayreuth.de

University of Bayreuth, Department of Chemical Engineering, Center of Energy Technology, Universitaetsstrasse 30, 95447 Bayreuth, Germany.

²Dr. Judith Scholz, Dr. Angela Heykamp
Evonik Performance Materials GmbH, Paul-Baumann-Strasse 1,
45772 Marl, Germany.

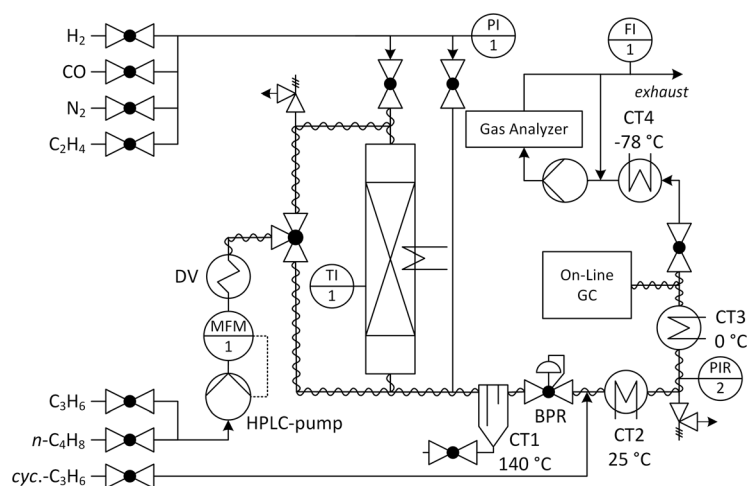


Figure 1. Experimental setup for FTS with co-feeding of C_2H_4 , C_3H_6 , and $n-C_4H_8$. MFM, mass flow meter; DV, direct vaporizer; CT, cold trap; BPR, back-pressure regulator; GC, gas chromatograph; PI, pressure indicator; TI, temperature indicator; FI, flow indicator.

conditions, and the bed temperature is controlled by an electrical heating jacket. The flow of the gases (H_2 , CO , N_2 , C_2H_4 , and a mixture of 1 % cyclopropane in N_2 , used as internal standard for the analysis by GC) is regulated by massflow controllers (Bronkhorst) and the pressure by a back-pressure regulator. C_3H_6 and C_4H_8 are liquids at reaction pressure (2 MPa) and ambient temperature, and are vaporized in a vaporizer (aDROP, aSTEAM DV-1) after raising their pressure to reaction pressure by an HPLC pump (Bronkhorst, mini CORIFLOW; FLUSYS WADose LITE HP).

The Mn-Co catalyst optimized for a high olefin selectivity (for preparation and characterization, see the Supporting Information) was activated in H_2 prior to FTS. The reactor containing the catalyst (4 g diluted 1:6 with quartz sand of 200–300 μm), was heated in a gas flow of 20 % H_2 in N_2 ($5 L_{STP} h^{-1} g_{cat}^{-1}$, $3 K min^{-1}$ to $360^\circ C$ with 3 h hold), then kept for 2 h at $360^\circ C$ in pure H_2 . After cooling to $150^\circ C$, the reactor was pressurized to reaction pressure (2 MPa) under syngas ($H_2/CO = 2 mol mol^{-1}$) and slowly heated to reaction temperature. To assure steady state, the catalyst was run for 50 h after activation and every change of the reaction conditions before sampling started. Repeated measurements showed no deactivation or selectivity change. Nevertheless, each parameter variation was carried out with a fresh catalyst.

All experiments, except for H_2 pressure variations, were carried with a H_2 -to- CO ratio of 2. N_2 was used as make-up to maintain a constant total pressure. The temperature for all experiments was $210^\circ C$ except for the variation of ethene pressure at $190^\circ C$ due to the high reactivity. By adjusting the residence time a constant CO conversion of about 10 % could be achieved, which guarantees differential conditions for calculation of reaction rates. The volume flows of the feed and product gas were measured in a soap bubble burette. For details on reaction conditions and analysis, see the Supporting Information.

2.2 Calculations

The conversion $X_i^{(1)}$ of CO and olefin was calculated using Eq. (1):

$$X_i = \frac{\dot{n}_{i,in} - \dot{n}_{i,out}}{\dot{n}_{i,in}} \quad (1)$$

with $i = CO$, olefin.

The reaction rates were calculated by Eq. (2).

$$r_i = \frac{\dot{n}_{i,in} - \dot{n}_{i,out}}{m_{Co}} \quad (2)$$

with $i = CO$, olefin.

The conversion-related carbon mass balance MB_C was determined to verify that all (> 90 %) of the converted carbon from CO and the co-fed olefins is found in the products $\dot{m}_{C,product}$:

$$MB_C = \frac{\dot{m}_{C,product}}{(\dot{m}_{C,CO,in} + \dot{m}_{C,Olefin,in}) - (\dot{m}_{C,CO,out} + \dot{m}_{C,Olefin,out})} \quad (3)$$

The modified residence time τ' is the ratio of the mass of the main active component cobalt and the total volume flow \dot{V}_{tot} under reaction conditions:

$$\tau' = \frac{m_{Co}}{\dot{V}_{tot}} \quad (4)$$

The experimental setup allows to measure the overall CO conversion only (rate $r_{CO,overall}$). To distinguish between CO consumed by standard FTS ($r_{CO,FTS}$) and by reaction with the co-fed olefin ($r_{CO,olefin}$), the experiments were carried out under the same conditions with and without olefin co-feeding. The rate of CO consumption by reaction with the olefin $r_{CO,olefin}$ was calculated based on the measurable overall rate $r_{CO,overall}$ and the FTS only rate $r_{CO,FTS}$ without olefin addition assuming that the olefin does not affect the surface concentration of other species above all of CO :

$$r_{CO,olefin} = r_{CO,overall} - r_{CO,FTS} \quad (5)$$

It must be noted that for the given reaction conditions, above all high partial pressures of the co-fed olefins, $r_{CO,overall}$ turned out to be much higher than $r_{CO,FTS}$ in case of ethene. For propene addition, $r_{CO,propene}$ is in the same order of magnitude as $r_{CO,FTS}$, and in case of butene addition, $r_{CO,butene} \ll r_{CO,FTS}$; see Sect. 3 and Fig. S1 in the Supporting Information. The assumption that $r_{CO,FTS}$, i.e., formation of HCs (only) from CO and H_2 , is not affected by olefin co-feeding is confirmed by the fact that the formation rates of HCs with lower carbon numbers as the one of the co-fed olefin (CH_4 for ethene, CH_4 and C_2 -HCs in case of propene, and CH_4 , C_2 -HCs and C_3 -HCs for butene)

1) List of symbols at the end of the paper.

are practically not affected by addition of ethene, propene, and butene, respectively (see Figs. S2–S4). Note that this simplification by separating the reaction pathways is not true on a mechanistic level where hydroformylation and FTS (with and without olefin co-feeding) are sharing common initiation reaction steps.

The carbon-related selectivity S_{methane} of FTS was calculated from the rate of methane formation $r_{\text{C,methane,FTS}}$ relative to the rate of CO conversion by FTS only, $r_{\text{CO,FTS}}$. For further information see Tab. S2.

$$S_{\text{methane}} = \frac{r_{\text{C,methane}}}{r_{\text{CO,FTS}}} \quad (6)$$

3 Results

3.1 Change of CO Reaction Rate by Co-Feeding of Olefins

A linear increase in the CO conversion rate was observed with rising olefin partial pressure while co-feeding C_2H_4 , C_3H_6 , and $n\text{-C}_4\text{H}_8$ (Fig. 2). This confirms the results of Adesina et al. for a low ethene partial pressure of about 0.02 bar compared to this work with 1 to 4 bar [14]. This increase in activity is most pronounced for ethene with an rise in activity of 25-fold at 4 bar C_2H_4 compared to FTS only. The activity increase is noticeably lower for C_3H_6 (2-fold) and $n\text{-C}_4\text{H}_8$ co-feeding (1.2-fold). This decrease of the enhancement of the rate with growing chain length of the olefin corresponds to results of co-feeding of ethene and propene in lower concentrations [7]. The probability of olefin (re)adsorption also seems to be reduced with increasing chain length [15]. It should be noted that the co-feeding experiments took place at different temperatures (190 °C and 210 °C) to avoid a temperature run-away in case of C_2H_4 . The measurements show that the relative activity is the same for these temperatures so the effects seen here can be ascribed solely to the difference in C-number of the co-fed olefin.

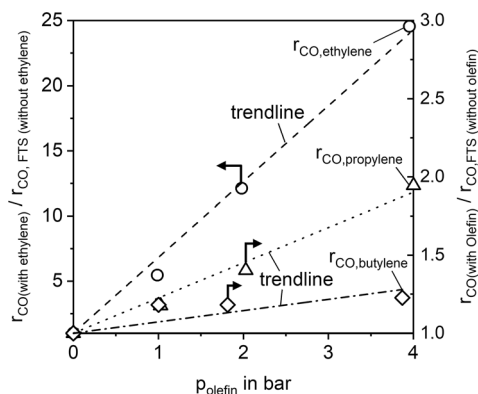


Figure 2. Normalized CO conversion rates with increasing partial pressure of ethene (190 °C, $r_{\text{CO,FTS}}$ (without ethene) = $0.54 \text{ mmol s}^{-1} \text{ kg}_{\text{CO}}^{-1}$), propene, and 1-butene (both 210 °C, $r_{\text{CO,FTS}}$ (without olefin) = $3.61 \text{ mmol s}^{-1} \text{ kg}_{\text{CO}}^{-1}$), olefin partial pressures 0 to 4 bar, $X_{\text{CO}} = \text{const.} \approx 10\%$.

An increasing olefin partial pressure also leads to increasing olefin conversion rates, but comparing the absolute values of CO and olefin conversion rates leads to a mismatch as shown for co-feeding of C_2H_4 in Fig. 3. The conversion of ethene (and also of the C_3 - and C_4 -olefin) is higher compared to the CO conversion. This could be due to hydrogenation, dimerization, and/or oligomerization of the olefin. Yet, product analyses and H_2 conversion rates confirm hydrogenation to the corresponding alkane to be the reason. Conversion of ethene varied from 60 % (at 1 bar C_2H_4) to 25 % (at 4 bar), but about 65 % of the converted ethene was always hydrogenated to ethane. Analogous observations were made for C_3H_6 and $n\text{-C}_4\text{H}_8$ with an even higher selectivity to the corresponding alkane (80–90 %).

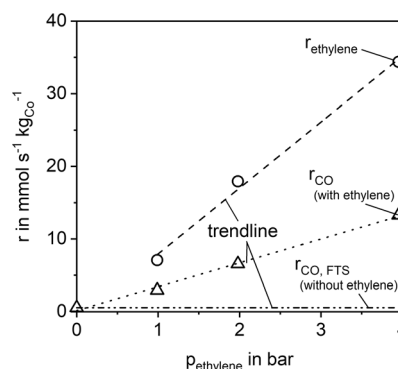


Figure 3. Conversion rates of ethene and CO with varying partial pressure of ethene (0 to 4 bar) and CO conversion rate for FTS without olefin co-feeding ($p_{\text{H}_2} = 6 \text{ bar}$, $p_{\text{CO}} = 3 \text{ bar}$, 190 °C, $X_{\text{CO}} = \text{const.} \approx 10\%$).

3.2 Product Composition at Varying Olefin Partial Pressures

Besides hydrogenation, up to 40 % of the co-fed olefin reacts with CO and H_2 to form linear higher alkanes and olefins, mainly 1-alkenes, or higher oxygenates (alcohols and aldehydes), as can be seen in Tab. 1. In case of ethene co-feeding, a maximum of 10–20 % of the converted olefin can be found in FTS products. The main products of all co-fed olefins are the corresponding alkane and oxo-products from hydroformylation (Figs. S5–S7). It should be noted that the amount of co-fed olefin was much higher than the amount produced by FTS so the latter one could be neglected.

The most significant change when co-feeding olefins occurs in the fractions with C-number N elongated by one (= C_3 for C_2H_4 -, C_4 for C_3H_6 -, and C_5 for C_4H_8 -co-feeding, in general: “ $N+1$ ”). Slight increases compared to FTS without co-fed olefins can be found in fractions with higher C-numbers as well, yet the dominating reaction is initiation of chain growth and not propagation, as shown in previous works [6, 16, 17].

Furthermore, while in mere FTS no aldehydes and very few alcohols are produced, co-feeding of olefins leads to a significant increase of these products. This is particularly pronounced for the “ $N+1$ ”-fraction: This fraction consists of 95 % valuable (non-paraffinic) products (olefins, aldehydes, alcohols) in case of co-feeding of ethene compared to 69 % without co-feeding.

Table 1. Relative increase of mass fractions of products with different carbon numbers for olefin co-feeding compared to mere FTS, i.e., without olefin addition, and composition of these fractions ($p_{\text{olefin}} = 2 \text{ bar}$, $p_{\text{H}_2} = 6 \text{ bar}$, $p_{\text{CO}} = 3 \text{ bar}$, $210 \text{ }^\circ\text{C}$, $X_{\text{CO}} = \text{const.} \approx 10 \%$).

C-number N	2	3	4	5	6	7	8
<i>Without co-fed olefin (mere FTS)</i>							
Alkanes [%]	68	31	37	38	42	50	63
Olefins [%]	12	58	49	47	43	32	19
Alcohols [%]	20	9	14	15	15	18	18
Aldehydes [%]	0	2	0	0	0	0	0
<i>Ethene co-feeding</i>							
Increase rel. mere FTS ^{a)} [%]		66	6	4	6	4	3
Alkanes [%]		5	20	20	38	35	29
Olefins [%]		22	77	79	60	63	69
Alcohols [%]		37	2	1	2	2	2
Aldehydes [%]		36	1	0	0	0	0
<i>Propene co-feeding</i>							
Increase rel. mere FTS ^{a)} [%]	-3		18	3	2	2	1
Alkanes [%]	50		11	37	31	46	40
Olefins [%]	18		17	55	41	29	25
Alcohols [%]	32		59	8	28	25	35
Aldehydes [%]	0		13	0	0	0	0
<i>1-Butene co-feeding</i>							
Increase rel. mere FTS ^{a)} [%]	-3	-7		11	3	2	2
Alkanes [%]	37	19		10	23	25	39
Olefins [%]	38	70		25	55	50	38
Alcohols [%]	25	7		50	22	25	23
Aldehydes [%]	0	4		15	0	0	0

^{a)} "Increase relative to mere FTS" means the additional amount of carbon found in a product fraction with C-number N compared to the case of FTS without olefin addition. For example; for ethene co-feeding, the amount of carbon found as C₃-species is 66 % higher compared to FTS without ethene addition. Note that the CO conversion was always kept constant (10 %) by respective variation of residence time. Nevertheless, the overall amount of the produced carbon species (HCs, oxoproducts) is always higher for olefin addition due to chain growth of the co-fed olefin to higher HCs by participation in the FTS, hydroformylation to aldehydes and alcohols by subsequent hydrogenation.

For propene and butene, the respective values are 89 % and 90 %, respectively, compared to 63 % and 62 % without olefin addition. Hence, not only the FTS reaction mechanism is active but also hydroformylation of the co-fed olefins to alcohols and aldehydes takes place, as already stated by Anderson for ethene co-feeding in Co-catalyzed FTS [18].

For C₄- and C₅-alcohols and aldehydes linear as well as the branched isomers were found (iso-butanol/iso-butanal,

2-methyl-1-butanol, 2-methyl-1-butanol). Interestingly, even with changing reaction conditions, the ratio of linear-to-branched isomers is always constant (Tab.S3), indicating that regioselectivity mostly depends on the catalyst. Similar effects were studied for other solid catalysts and a variety of reactions [19].

Since the main effect takes place in the product fraction $N+1$ only these fractions are considered further in this work. In Figs. 4 and 5, the composition of the C₃- and C₄-fractions when adding different amounts of C₂H₄ and C₃H₆ to the FTS is shown. The addition of C₄H₈ hereby gives results analogous to C₃H₆ co-feeding and therefore is not mentioned here.

The addition of olefins leads to a highly decreased share of alkanes and olefins in the $N+1$ -fraction compared to FTS only. This is not the result of reduced production rates of those components but originates from the enhanced synthesis rate of the corresponding oxo-products. This effect is more visible for ethene co-feeding with an increase in C-mass of the C₃-fraction of 66 % compared to FTS only (Tab.1) than for propene and 1-butene (18 wtC % increase in C₄-fraction and 11 wtC % increase in C₅-fraction).

In general, tendencies of the change of the composition in the $N+1$ -fraction are similar for all three olefins (Figs. 4 and 5). While the fraction of produced alkanes and olefins remains fairly unchanged, an increase in olefin pressure leads to a higher aldehyde content at the expense of the alcohol. The increasing H₂ conversion for higher olefin partial pressure leads to a lower concentration of H₂ (Tab.2). While the aldehyde is the primary product of hydroformylation, the corresponding alcohol results from subsequent aldehyde hydrogenation. A lower H₂ concentration thus reduces hydrogenation, shifting the product composition to the aldehyde.

This effect is more pronounced for ethene co-feeding than for longer olefins. While propene addition leads to a decrease of butanol content in the C₄-fraction, 60 % at 1 bar C₃H₆ to 54 % at 4 bar (Fig. 5), equal

amounts of ethene result in a change of the alcohol content in the C₃-fraction from 40 % to almost 0 % (Fig.4). An explanation is the difference in temperature. Due to the high reactivity of C₂H₄ those experiments were carried out at 190 °C, while propene co-feeding took place at 210 °C. Roelen also stated that higher temperatures lead to aldehydes and lower ones to alcohols as preferred products of hydroformylation [10].

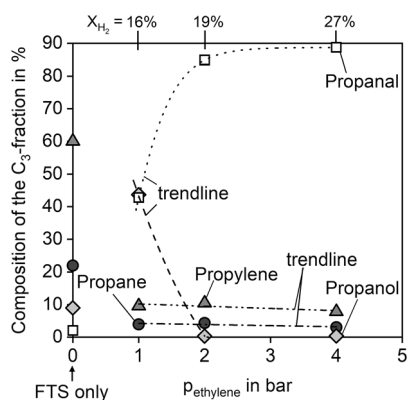


Figure 4. Composition of C₃-fraction for a partial pressure of ethene from 0 to 4 bar ($p_{\text{H}_2} = 6$ bar, $p_{\text{CO}} = 3$ bar, 190 °C, $X_{\text{CO}} = \text{const.} \approx 10\%$).

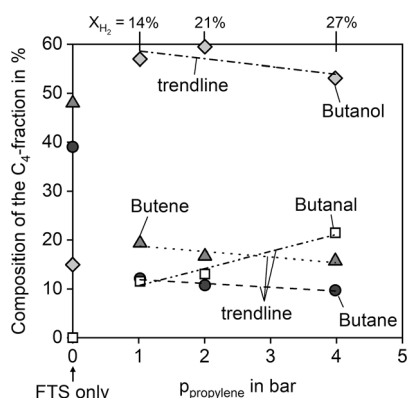


Figure 5. Composition of C₄-fraction for a partial pressure of propene from 0 to 4 bar ($p_{\text{H}_2} = 6$ bar, $p_{\text{CO}} = 3$ bar, 210 °C, $X_{\text{CO}} = \text{const.} \approx 10\%$).

Table 2. Conversion of olefin and H₂ at olefin partial pressures from 1 to 4 bar ($p_{\text{H}_2} = 6$ bar, $p_{\text{CO}} = 3$ bar, $T_{\text{reaction}} = 190$ °C for C₂H₄ and 210 °C for C₃H₆/C₄H₈), $X_{\text{CO}} = \text{const.} \approx 10\%$.

p_{olefin} [bar]	1	2	4
<i>Ethene co-feeding</i>			
X_{ethene} [%]	62	42	26
X_{H_2} [%]	16	19	27
<i>Propene co-feeding</i>			
X_{propene} [%]	9	11	8
X_{H_2} [%]	14	21	27
<i>1-Butene co-feeding</i>			
$X_{1\text{-butene}}$ [%]	6	8	8
X_{H_2} [%]	14	14	15

Besides small amounts of olefin that can be found when co-feeding ethene, all experiments with co-feeding of an olefin (with carbon number N) clearly show that the olefin is practi-

cally only converted to the corresponding paraffin by hydrogenation or to oxo-products (mainly with carbon number $N+1$) by hydroformylation (see Figs. S5–S7).

3.3 Product Composition at Varying H₂ Partial Pressure

As stated before, the most dominant reaction of the co-fed olefins is the undesirable hydrogenation to the corresponding alkanes. Past studies therefore tried to avoid hydrogenation by keeping either the C₂H₄ content low or by reducing the H₂ pressure [14, 20]. Thus, a variation of the H₂ pressure was carried out in order to suppress hydrogenation by a lack of H₂. In case of C₃H₆ and n -C₄H₈ co-feeding, it was not possible to reduce the selectivity of hydrogenation to less than 70 % (Fig. 6). In case of ethene, hydrogenation could significantly be reduced from 70 % to 50 % at low H₂ pressures where a high or even full conversion of H₂ was reached at the end of the catalyst bed. Hence, 50 % of the (converted) co-fed ethene reacts to valuable compounds such as alcohols or aldehydes at best. A further decrease of the H₂ pressure is then not possible without risking catalyst deactivation by carbonaceous deposits due to lack of H₂.

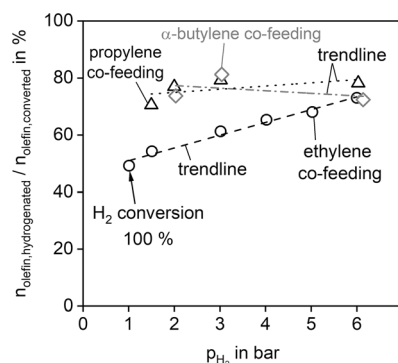


Figure 6. Quantity of hydrogenated olefin in relation to the amount of olefin converted in total at varying H₂ partial pressures from 1 to 6 bar ($p_{\text{olefin}} = 2$ bar, $p_{\text{CO}} = 3$ bar, 210 °C, $X_{\text{CO}} = \text{const.} \approx 10\%$).

Furthermore the compositions of the $N+1$ -fractions were investigated at varied H₂ partial pressures. Fig. 7 presents the change of the C₃-fraction at C₂H₄ co-feeding. The results for C₃H₆ and n -C₄H₈ are analogous and not displayed here. Within the C₃-fraction, an increasing H₂ pressure leads to a slightly rising share of propane at the expense of propene (Fig. 7). This is due to the increased rate of hydrogenation of C₃H₆ at higher H₂ partial pressures. A more significant effect is seen for the oxo-products propanol and propanal. At less than 2 bar H₂ partial pressure the share of propanal is 90 %, but this changes with increasing H₂ pressure until at 6 bar there are equal amounts of both. As already mentioned, the aldehyde is the primary product of hydroformylation and hydrogenation to the alcohol strongly depends on H₂.

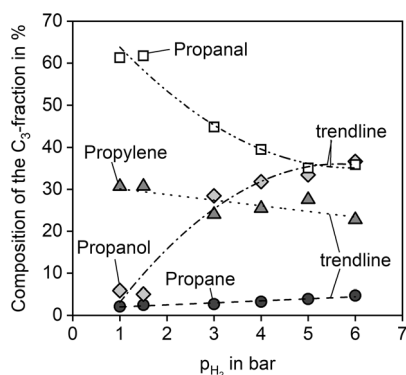


Figure 7. Composition of C_3 -fraction at ethene co-feeding at varying partial pressure of H_2 from 1 to 6 bar ($p_{CO} = 3$ bar, $p_{ethene} = 2$ bar, $210^\circ C$, $X_{CO} = \text{const.} \approx 10\%$).

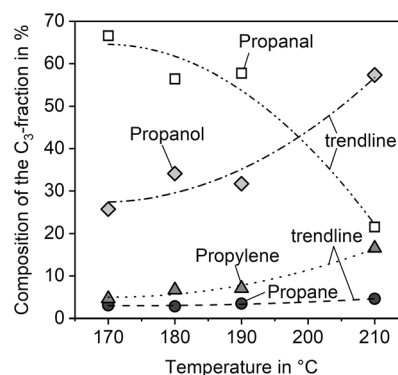


Figure 9. Composition of the C_3 -fraction at ethene co-feeding for a temperature range of 170 to $210^\circ C$ ($p_{ethene} = 2$ bar, $p_{H_2} = 6$ bar, $p_{CO} = 3$ bar, $X_{CO} = \text{const.} \approx 10\%$).

3.4 Variation of Reaction Temperature

The effect of temperature on FTS, hydroformylation, and hydrogenation was studied in a range from 170 to $210^\circ C$. Due to its high reactivity compared to propene and butene, ethene was used as co-feed. The reaction rates of ethene and CO are indicated in Fig. 8. The rate of CO was split into the amount of consumed by FTS and by reaction with C_2H_4 . As expected, the rates strongly increase with temperature. Compared to CO consumed by reaction with ethene (and H_2) the FT reaction (reaction of CO and H_2 ; rate $r_{CO,FTS}$) can be neglected and is below the detection threshold at temperatures below $190^\circ C$.

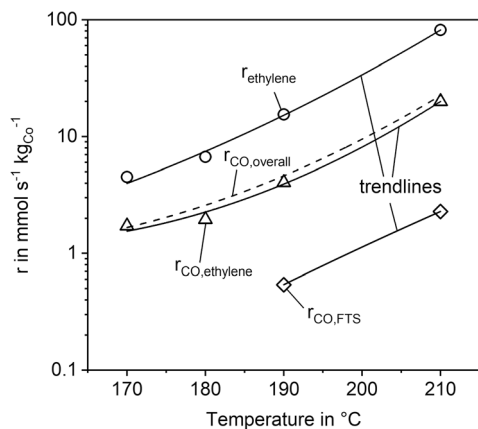


Figure 8. Influence of temperature on reaction rates (logarithmic scale) of ethene ($r_{ethylene}$), of CO consumed by reaction with ethene by FTS (reaction of C_2H_4 with CO and H_2 ; rate $r_{CO,ethylene}$), and of CO consumed by mere FTS (reaction of CO only with H_2 ; $r_{CO,FTS}$). Dashed line represents rate of overall CO consumption ($r_{CO,overall} = r_{CO,ethylene} + r_{CO,FTS}$) (conditions: $p_{ethene} = 2$ bar, $p_{H_2} = 6$ bar, $p_{CO} = 3$ bar, $X_{CO} = \text{const.} \approx 10\%$).

The composition of the C_3 -fraction at different temperatures is illustrated in Fig. 9. While a decrease of temperature almost has no effect on the share of propane in the C_3 -fraction and only leads to a slight decline in propene, the effect on propanol and propanal is significant. While at $210^\circ C$ the oxygenated

compounds consist primarily of propanol (75 %) and only 25 % propanal, these values invert at lower temperatures, and at $170^\circ C$ the aldehyde accounts for 75 % of the oxo-products. This matches the results of Roelen who described a certain “critical” temperature (100– $140^\circ C$ for a Co-catalyst on kieselgur). Below this temperature, carbonyl compounds are preferred while above alcohols become predominant [10].

The selectivity for hydrogenation of C_2H_4 remains fairly constant at 70 % for temperatures between 180 and $210^\circ C$ but drops significantly to 62 % at $170^\circ C$ (Fig. 10). Hence, hydrogenation at lower temperatures is less favored than hydroformylation and thus a possibility to reduce the undesirable alkane production to a certain extent.

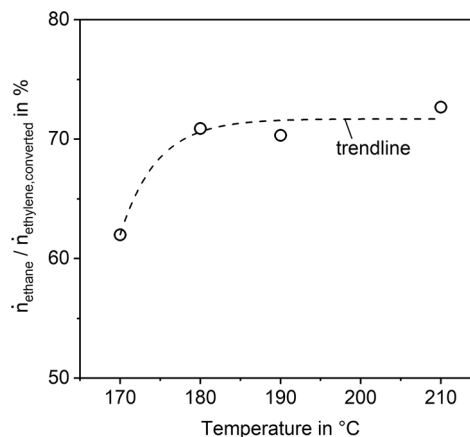


Figure 10. Quantity of hydrogenated ethene in relation to the amount of ethene converted in total in a temperature range of 170 to $210^\circ C$ ($p_{ethene} = 2$ bar, $p_{H_2} = 6$ bar, $p_{CO} = 3$ bar, $X_{CO} = \text{const.} \approx 10\%$).

4 Conclusion

Co-feeding of ethene, propene, and 1-butene leads to a strong increase of the CO reaction rate. This effect is most visible at ethene co-feeding and significantly decreases with increasing chain length of the co-fed olefin. For co-feeding olefins, several

reactions were observed. The most dominant reaction is the hydrogenation of the olefin and makes up 50–90 % of the converted olefin. The second main reaction is hydroformylation of the olefin to oxo-products elongated by only one carbon atom, which makes up 10–40 % of the converted olefin. This leads to a high selectivity for short-chained alcohols and aldehydes. The remaining, small share of converted olefin seems to function as a chain initiator for common FTS reactions. This results in elongation of the co-fed olefin by one or more carbon atoms whereby chain growth follows the common Anderson-Schulz-Flory distribution for FTS.

A decrease of the H₂ pressure leads to a shift from alcohols to aldehydes. Raising the partial pressure of the co-fed olefins also leads to a shift of the oxygenated products to aldehydes as well as to an increased conversion of H₂ by hydrogenation of the olefin. The reason for the shift within the oxo-products is probably in both cases a lack of H₂ needed for the aldehyde hydrogenation to the alcohol.

Temperatures above 200 °C favor the formation of the alcohol whereas lower temperatures lead to the aldehyde as favored product.

The selectivity for olefin hydrogenation seems, especially for C₂H₄, to depend on the H₂ partial pressure and temperature. A reduction of the H₂ partial pressure leads to a decrease in ethane selectivity as well. Yet even at low H₂ pressures resulting in full conversion of H₂ at the end of the catalyst bed, a reduction of the ethane selectivity below 50 % was not possible. Further studies should consider a catalyst screening to achieve higher selectivities for hydroformylation or FTS, depending on whether olefins or oxygenated compounds are the preferred product and reduce the share of olefin hydrogenation.

Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/ceat.202100488>. This section includes an additional reference to primary literature relevant for this research [21].

Acknowledgment

The authors thank Evonik Performance Materials GmbH for financial support. Open access funding enabled and organized by Projekt DEAL.

The authors have declared no conflict of interest.

Symbols used

d	[m]	diameter
m	[kg]	mass
\dot{m}	[kg s ⁻¹]	mass flow
MB	[-]	conversion-related mass balance
N	[-]	carbon number
\dot{n}	[mol s ⁻¹]	molar flow
p	[Pa]	partial pressure

r	[mol s ⁻¹ kg _{Co} ⁻¹]	reaction rate
S	[-]	selectivity
T	[°C, K]	temperature
\dot{V}	[m ³ s ⁻¹]	volume flow
X	[-]	conversion

Greek letter

τ	[kg _{Co} s m ⁻³]	modified residence time
--------	---------------------------------------	-------------------------

Sub- and superscripts

C	carbon
Co	cobalt
i	compound i
p	particle

Abbreviations

CT	cold trap
FTS	Fischer-Tropsch synthesis
GC	gas chromatography
HC	hydrocarbon
HPLC	high-performance liquid chromatography
TOS	time-on-stream

References

- [1] H. Schulz, *Top. Catal.* **2003**, *26* (1–4), 73–85. DOI: <https://doi.org/10.1023/B:TOCA.0000012988.86378.21>
- [2] F. Fischer, H. Tropsch, *Brennst.-Chem.* **1923**, *4*, 276–285.
- [3] P. Kaiser, R. B. Unde, C. Kern, A. Jess, *Chem. Ing. Tech.* **2013**, *85* (4), 489–499. DOI: <https://doi.org/10.1002/cite.201200179>
- [4] H. Schulz, M. Claeys, *Appl. Catal., A* **1999**, *186*, 71–90. DOI: [https://doi.org/10.1016/S0926-860X\(99\)00165-9](https://doi.org/10.1016/S0926-860X(99)00165-9)
- [5] H. Schulz, B. R. Rao, M. Elstner, *Erdoel Erdgas Kohle* **1970**, *23*, 651–655.
- [6] R. Snel, R. L. Espinoza, *J. Mol. Catal.* **1987**, *43* (2), 237–247. DOI: [https://doi.org/10.1016/0304-5102\(87\)87011-6](https://doi.org/10.1016/0304-5102(87)87011-6)
- [7] R. Snel, R. L. Espinoza, *J. Mol. Catal.* **1989**, *54* (1), 103–117. DOI: [https://doi.org/10.1016/0304-5102\(89\)80143-9](https://doi.org/10.1016/0304-5102(89)80143-9)
- [8] Y. Zhang, Y. Yao, J. Shen, J. Chang, J. Gorimbo, X. Liu, D. Hildebrandt, *Fuel* **2021**, *302*, 121146. DOI: <https://doi.org/10.1016/j.fuel.2021.121146>
- [9] I. Zhou, J. Gao, X. Hao, Y. Yang, Y. Li, *Reactions* **2021**, *2*, 161–174. DOI: <https://doi.org/10.3390/reactions2020012>
- [10] O. Roelen, *German Patent 2 327 066*, **1943**.
- [11] *Chemical Technology* (Eds: A. Jess, P. Wasserscheid), 2nd ed., Wiley-VCH, Weinheim **2020**.
- [12] D. Schroeder, Herstellung kurz- und mittelkettiger Olefine durch Fischer-Tropsch-Synthese, *Ph.D. Thesis* (submitted), University of Bayreuth, **2021**.
- [13] D. Schröder, J. Thiessen, A. Jess, J. Scholz, *Catal. Sci. Technol.* **2020**, *10* (2), 475–483. DOI: <https://doi.org/10.1039/c9cy02022e>
- [14] A. A. Adesina, R. R. Hudgins, P. L. Silveston, *Appl. Catal.* **1990**, *62* (1), 295–308. DOI: [https://doi.org/10.1016/S0166-9834\(00\)82253-8](https://doi.org/10.1016/S0166-9834(00)82253-8)

- [15] E. W. Kuipers, I. H. Vinkenburg, H. Oosterbeek, *J. Catal.* **1995**, *152* (1), 137–146. DOI: <https://doi.org/10.1006/jcat.1995.1068>
- [16] Y. T. Eidus, *Russ. Chem. Rev.* **1967**, *36* (5), 338–351. DOI: <https://doi.org/10.1070/RC1967v036n05ABEH001628>
- [17] O. A. Golovina, M. M. Sakharov, S. Z. Roginskii, E. S. Dokukina, *Russ. J. Phys. Chem.* **1959**, *33*, 471.
- [18] R. B. Anderson, *The Fischer-Tropsch Synthesis*, Academic Press, New York **1984**.
- [19] V. Dal Santo, M. Guidotti, R. Psaro, L. Marchese, F. Carniato, C. Bisio, *Proc. R. Soc. A* **2012**, *468* (2143), 1904–1926. DOI: <https://doi.org/10.1098/rspa.2012.0056>
- [20] S. C. Chuang, J. G. Goodwin Jr., I. Wender, *Prepr. – Am. Chem. Soc., Div. Pet. Chem.* **1984**, *29* (4), 1108.
- [21] G. J. Hutchings, R. G. Copperthwaite, M. van der Ried, *Top. Catal.* **1995**, *2*, 163–172.