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Hydrocracking of Model Substances on Pt/H-ZSM-5 under an Imitated Fischer-Tropsch Product Gas Composition

Combining Fischer-Tropsch synthesis (FTS) and subsequent cracking of unwanted long-chain primary FT products in a tandem process is a successful procedure to improve the selectivity towards liquefied petroleum gas (LPG). To simplify the process, both reactions are carried out consecutively without prior product separation after FTS. In this work, the gas composition after FTS is imitated and, thus, the influence of unreacted CO and the by-product water on the hydrocracking of *n*-hexadecane as model substance is investigated. Furthermore, the reaction of alcohols and LPG components on a bifunctional Pt/H-ZSM-5 zeolite was examined as they are typically found in FT products. The cracking is affected negatively by the presence of CO, which is why a product separation upstream of hydrocracking after FTS can be considered as useful.

Supporting Information available online

Keywords: Fischer-Tropsch synthesis, Hydrocracking, Liquefied petroleum gas, Product separation, Tandem processes

Received: April 17, 2023; *revised:* June 01, 2023; *accepted:* June 09, 2023

DOI: 10.1002/ceat.202300203

1 Introduction

The Fischer-Tropsch synthesis (FTS) plays a major role in the large-scale production of hydrocarbons (HCs) from syngas ($CO + H_2$) in the so-called gas-to-liquid process. By the use of renewable hydrogen by water electrolysis and CO_2, the latter may be obtained by separation from exhaust gases of power plants, the cement or chemical industry, or in the future by direct air capture. Such a process can help to reduce anthropogenic greenhouse gas emissions and thus mitigate the effects of climate change [1–5]. Prior to FTS, CO_2 has to be transformed to CO by the reverse water-gas shift reaction.

In Wunsiedel, a small city in Upper Franconia (northern Bavaria), one of the largest water electrolyzers in Europe was put into operation in September 2022. The annual capacity is 1350 t of green hydrogen [6]. In addition to direct use, the produced hydrogen can be converted to HCs by means of FTS. To meet the demand of liquefied petroleum gas (LPG) in this rural area as fuel in households or small businesses, it is of great interest to enhance the selectivity of LPG in a tandem process combining FTS and subsequent hydrocracking. First results were recently presented [7].

The FTS can be regarded as a surface catalyzed polymerization with a statistical distribution of the mainly linear hydrocarbons (HCs), known as Anderson-Schulz-Flory distribution (ASF), characterized by the chain growth probability α [8–10]. This drawback limits the use of FTS since it is impossible to selectively produce one hydrocarbon or a hydrocarbon cut with a narrow carbon number distribution.

To overcome this limitation and increase, e.g., the selectivity to LPG, downstream processing of the primary longer-chain FT compounds by means of cracking on an acidic zeolite is an option [11–15]. Combining FT catalysts and zeolite catalysts in a single-step (hybrid concept) for an improved selectivity to gasoline range hydrocarbons has been attempted by many groups, using the following strategies: (1) zeolite-supported FT catalysts [16, 17], (2) physically mixing or layering both catalysts [18–21], and (3) zeolite encapsulated FT catalysts [22–24]. Since the single-step process suffers from the disadvantage that one catalyst must operate under less than optimal conditions, many combinations of a two-stage process (FT catalyst and zeolite catalyst are separated) have been tested focusing on a high yield of gasoline [25–30]. To our best knowledge, there is only little research done to enhance the selectivity of LPG in an FTS/hydrocracking process [15, 31], as LPG is often regarded as low-value product compared to gasoline or diesel oil.

What has to be considered in all these attempts is the fact that the gas composition for hydrocracking is directly related to the FT reaction, meaning that non-reacted carbon monoxide as well as the FT by-product water are present. Besides long-chain aliphatics, which have to be cracked to LPG (C_3 and C_4

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hydrocarbons (HCs)), also primary alcohols and LPG components already formed by FTS are present at the zeolite. A schematic presentation of the tandem process with the gas components present downstream of FTS is shown in Fig. 1.

There are already some studies investigating the cracking reaction of paraffins under the influence of CO and they saw a negative effect [20, 32]. Also, the reaction of model olefins of different chain length has been investigated and revealed that CO poisoning of the (de)hydrogenation functionality of the hydrocracking catalyst leads to divergences of the reaction pathways compared to typical hydrocracking conditions (without presence of CO) [33]. Also, the addition of water seems to influence cracking via competitive adsorption on the acidic sites of the zeolite [34, 35].

The key objective of this work is to investigate the influence of CO and H_2O on the hydrocracking of the model hydrocarbon *n*-hexadecane at high temperature (350 °C) with regard to enhance the yield of LPG. Hence, the product gas of FTS was deliberately simulated by using different mixtures of the model HC (*n*-hexadecane), H_2, CO, and H_2O to study the effect of each compound separately, i.e., independent of the upstream FTS. Furthermore, the reactions of other FT products, namely, LPG components (propene, propane, *n*-butane, and 1-butene) and also alcohols, during hydrocracking on the zeolite were also investigated with and without the presence of CO. All these investigations are important to optimize and maximize the overall yield of LPG in a tandem process. The results should also show whether it is useful to modify the two-stage process of FTS and subsequent hydrocracking by the installation of a product separation downstream of FTS.

2 Experimental Section

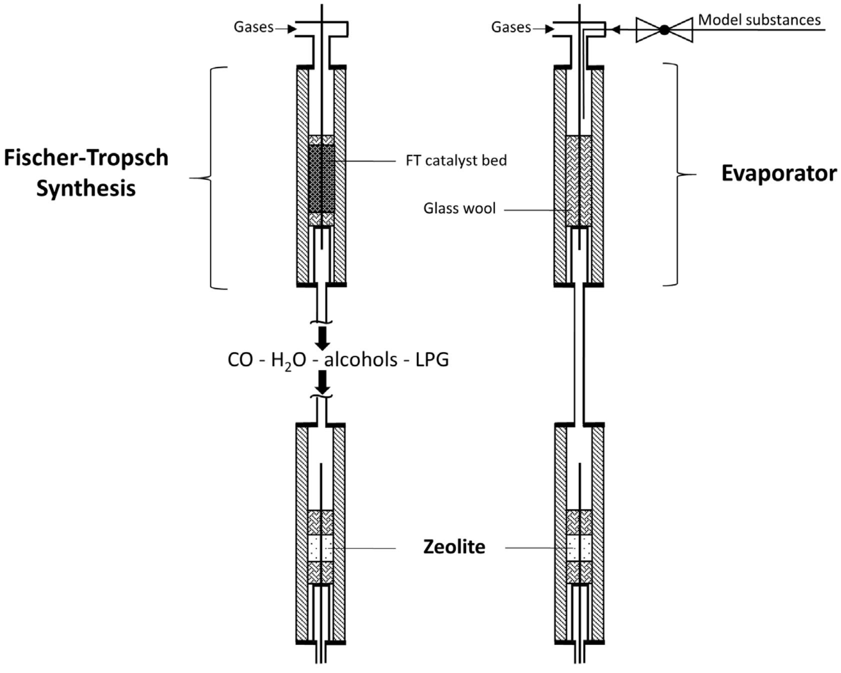
2.1 Zeolite Preparation

For all experiments, an H-ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 30 was used (D_{50} = 5 µm). For experiments with platinum as active metal, an ion exchange method was used to impregnate the H-ZSM-5 with 0.5 wt % Pt (content of Pt on final zeolite). In all other cases, the pure H-ZSM-5 catalyst was used without any addition of Pt. For a detailed description of the preparation of the catalyst see our previously published paper [7]. The acidity of the Pt/H-ZSM-5 zeolite was confirmed by NH_3-temperature-programmed desorption (TPD) measurements showing two distinct NH_3 desorption peaks, indicating acid centers on the catalyst surface (see Fig. S5 of the Supporting Information).

2.2 Reactor Setup

All experiments were conducted in stainless-steel fixed-bed reactors (d = 14 mm, l = 0.6 m) enclosed by an aluminum block to ensure isothermal conditions. Both reactors were heated by an electrical furnace and the temperature of the catalyst was monitored by thermocouples, located in thermocouple guide tubes (d = 3.0 mm). The reactors were arranged as tandem setup with two independently heatable reactors installed in series. The upper reactor (350 °C), where FTS would be conducted in a "real" tandem process, was filled with glass wool and served as vaporizer to evaporate the liquid model substances, e.g., *n*-hexadecane. Hence, the gaseous mixture of model HCs, H_2, CO, and H_2O represent the product gas of FTS and were then passed through the zeolite located in the lower hydrocracking reactor. The required gas flow was adjusted by Bronkhorst mass flow controllers.

For product analysis, the product gas of the hydrocracking reactor passed a trap (180 °C), maintained at reaction pressure (here 20 bar), to condense potentially occurring/remaining long-chain HCs. The pressure was subsequently relieved to ambient pressure and the gas stream was bubbled through a wash bottle kept at 0 °C and filled with toluene, to condense and wash out longer HCs not already condensed in the (hot) trap. These products were collected for 4–6 h and quantified by gas chromatography (GC) using cyclooctane as internal standard (liquid sample). The remaining gas stream was mixed with



a) "Real" Tandem Reactor **b) Reactor Setup**

Figure 1. (a) Schematic illustration of a "real" tandem reactor setup of a combined FTS/cracking process. Compounds appearing in the gas phase after FTS that may influence the hydrocracking process are highlighted and were therefore investigated in this work. (b) Reactor setup used in this investigation, where the upper reactor served as evaporator for model substances to mimic the gas phase after FTS.

1.5 L h^{-1} cyclopropane (1 vol % in N_2, internal standard for gas phase) and also analyzed by GC (gaseous sample). The gases (CO, CO_2, H_2) that cannot be measured by GC were analyzed by a gas analyzer after passing a final cold trap (–80 °C), which was installed to protect the instrument.

2.3 Catalytic Experiments

All catalysts, regardless of their composition, were treated in the same way prior to the start of the hydrocracking reaction. The zeolite was heated to 360 °C (3 K min^{-1}) with 3 h hold (20 vol % H_2 in N_2). The gas composition was then changed to pure hydrogen and kept at 360 °C for another 2 h; sufficient hydrogen was present for the complete reduction of the metal component. The temperature was then lowered to the reaction temperature of 350 °C for all experiments. This temperature was chosen, as previous experiments in a combined FTS/cracking process showed the highest selectivity for LPG [7]. The reactors were pressurized to 20 bar with the appropriate gas and the HPLC pump (KNAUER Smartline Pump 100) was started to adjust the desired flow of model substances (*n*-hexadecane or 1-butanol) into the evaporator. For experiments with H_2O, a second HPLC pump was installed to feed the previously calculated amount of water with the *n*-hexadecane simultaneously into the same evaporator. In all experiments with LPG as model substances (propene, propane, 1-butene, *n*-butane), the pump was cooled to –20 °C to avoid unwanted premature evaporation during the pumping process. A run-in period of 24 h was held after every change of reaction conditions.

In all of our experiments, we could determine a coking of the catalyst, which depends on the selected conditions and used model substance. However, long-term experiments showed that the coke formation did not significantly change the activity or selectivity of the used catalysts. Figs. S6 and S7 depict the conversion and cracking selectivities of *n*-decane cracking on H-ZSM-5 0.5 % Pt and pure H-ZSM-5 in syngas atmosphere.

2.4 Calculations

The conversion X_i for the used HCs was calculated using Eq. (1):

$$X_\mathrm{i} = \frac{\dot{n}_\mathrm{i;in} - \dot{n}_\mathrm{i;out}}{\dot{n}_\mathrm{i;in}} = \frac{\dot{m}_\mathrm{C,i;in} - \dot{m}_\mathrm{C,i;out}}{\dot{m}_\mathrm{C,i;in}} \tag{1}$$

with *i* = *n*-hexadecane, *n*-butanol, propane, propene, 1-butene, or *n*-butane.

The (de)hydrogenation conversion of propene, propane, 1-butene, and *n*-butane was calculated by Eq. (2):

$$X_\mathrm{i,(de)hydrogenation} = \frac{\dot{n}_\mathrm{j;out}}{\dot{n}_\mathrm{i;in}} \tag{2}$$

with *i* = used LPG component and *j* = corresponding (de)hydrogenated products with same carbon number.

The carbon-related selectivity $S_\mathrm{m,i}$ for the reaction products of the conversion of *n*-hexadecane and *n*-butanol was determined by Eq. (3):

$$S_\mathrm{m,i} = \frac{\dot{m}_\mathrm{C,i}}{\dot{m}_\mathrm{C,total}} \tag{3}$$

with *i* = carbon number of HC or carbon fraction, e.g., $C_{3+4} = C_3 + C_4$.

The molar selectivity $S_\mathrm{n,i}$ for the reaction products of the conversion of propane, propene, 1-butene, and *n*-butane was calculated by Eq. (4):

$$S_\mathrm{n,i} = \frac{\dot{n}_\mathrm{i}}{\dot{n}_\mathrm{total}} \tag{4}$$

The modified residence time $\tau^{*}_\mathrm{zeolite}$ is defined as:

$$\tau^{*}_\mathrm{zeolite} = \frac{m_\mathrm{zeolite}}{\dot{V}_\mathrm{total}(\mathrm{p,T})} \tag{5}$$

The carbon mass flow $\dot{m}_\mathrm{C,i}$ of each component *i* is given by Eq. (6):

$$\dot{m}_\mathrm{C,i} = \dot{m}_\mathrm{C,i;gas} + \frac{m_\mathrm{C,i;liq.}}{t_\mathrm{collection}} \tag{6}$$

with $t_\mathrm{collection}$ being the time of product collection.

The olefin/paraffin ratio was calculated by means of Eq. (7):

$$O/P = \frac{\sum \dot{m}_\mathrm{C;Olefins}}{\sum \dot{m}_\mathrm{C;Paraffins}} \tag{7}$$

3 Results and Discussion

3.1 Influence of Carbon Monoxide on the Cracking of *n*-Hexadecane as Model Substance (0.5 wt % Pt)

n-Hexadecane was used as a model substance for cracking experiments imitating C_{5+} hydrocarbons typically formed as primary FT products. Fig. 2a depicts the conversion of *n*-hexadecane and Fig. 2b the resulting olefin/paraffin ratio for a variation of the modified residence time. Under standard hydrocracking conditions (H_2 only, i.e., no CO and no H_2O), the conversion increased with increasing modified residence time reaching full conversion at 1.75 kg$_\mathrm{zeolite}$h m^{-3}. Almost all products were paraffins, indicating an efficient hydrogenation activity of Pt for hydrogenating olefinic cracking intermediates. Therefore, the corresponding O/P is very low and, with increasing residence time converges towards the thermodynamic equilibrium, which is almost zero under the used reaction conditions [36].

In the presence of CO in the simulated FT product gas stream (p_CO = 6.5 bar) the cracking activity and thus the conversion of *n*-hexadecane drops significantly (about 30 % absolute on average). Also, the O/P ratio is significantly higher in the presence of CO and far from equilibrium. Olefins are the primary cracking products leaving the acidic centers of the zeolite. Both the lower overall reaction rate and the higher O/P ratio can be attributed to partial poisoning of the (de)hydrogenation sites on Pt in bifunctional hydrocracking. The reactant (*n*-hexadecane) is first dehydrogenated on the metal sites

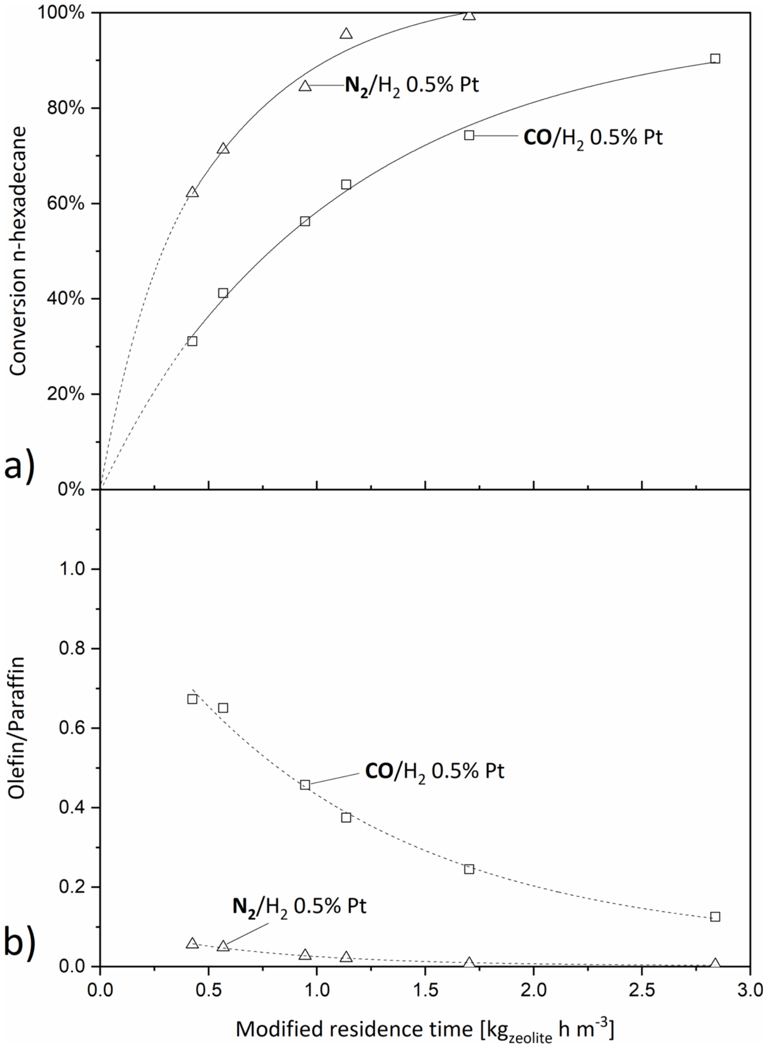


Figure 2. (a) Conversion of *n*-hexadecane for experiments with CO and additional experiments where CO is substituted by N_2, depending on the modified residence time. (b) In addition, the corresponding olefin/paraffin ratios are shown. For both series of experiments the same batch of catalyst (0.5 wt % Pt) and reaction conditions were used (p_{total} = 20 bar, p_{H2}/p_{CO} = 2 (without N_2) or p_{H2}/p_{N2} = 2 (without CO), $p_{n\text{-hexadecane}}$ = 0.5 bar, $m_{\text{zeolite (H-ZSM-5, 0.5 wt \% Pt)}}$ = 0.97 g, T = 350 °C).

of the catalyst forming olefins (*n*-hexadecene) and then protonated by the acid sites of the zeolite to carbenium ions which can undergo rearrangements or cracking reactions [37]. The hydrogen transfer to form these carbocations is the rate-determining step in the cracking mechanism. Although the olefin content is relatively low due to thermodynamics, in the best case it is high enough so that there are always enough olefins for the reaction. In the presence of CO, the cracking reaction rate of the catalyst decreased which can be attributed to the partial poisoning of the Pt sites, decreasing the number of metal centers available for the dehydrogenation of n-hexadecane.

Fig. 3 illustrates the product distribution as a function of *n*-hexadecane conversion. In the presence of CO, the selectivity of C_3 and C_4 compounds (LPG) improves with increasing conversion, due to enhanced secondary cracking of the C_{5+} HCs (Fig. 3a). Hence, the selectivity to these longer-chain compounds decreased with increasing *n*-hexadecane conversion. Furthermore, CH_4 and C_2 are present among the products. Since no HCs $< C_3$ are formed in the bimolecular cracking via carbenium ions on bifunctional catalysts, further cracking reactions took place in which C_1 and C_2 compounds are formed (superimposed monomolecular cracking via carbonium ions, also called Haag-Dessau cracking [38] or hydrogenolysis). Their selectivity increased due to the higher residence time of the reactants at the zeolite and a higher level of hexadecane conversion, respectively. The product distribution for the cracking reaction under “normal” (ideal) hydrocracking conditions (only H_2 without CO) is illustrated in Fig. 3b.

In contrast to the experiments with CO, there is no strong dependence of the C_{3+} selectivity on the conversion of *n*-hexadecane. The reason for this is the low olefin partial pressure without CO, i.e., the (de)hydrogenation activity of Pt is unaffected. Thus, there is no competitive adsorption at the acidic centers and the adsorbed compounds are subjected to increased secondary cracking due to the longer residence time at the active sites. The formation of C_1 and C_2 compounds appears to be independent of the presence of CO, since the selectivities to these compounds are the same (for a given conversion of hexadecane) in both series of experiments.

Tab. 1 presents the influence of the partial pressure of CO on the selectivity of the cracking reactions. Furthermore, the required residence time is given, which had to be adjusted to achieve a constant conversion of n-hexadecane (here 55 %). After the addition of CO, the adjusted residence time increased linearly with rising partial pressure of CO. This confirmed the assumption that CO has a negative effect on the cracking activity by partially blocking the Pt sites, i.e., CO adsorbs strongly on Pt. The selectivity to methane or C_2 HCs does not significantly change with increasing CO partial pressure. Looking at the C_{3+} compounds, there is a slight decrease in C_3/C_4 selectivity with a simultaneous increase in C_{5+} selectivity with increasing partial pressure of CO. Note that the residence time also had to be increased to keep the *n*-hexadecane conversion constant.

The addition of CO led to a strong increase in the O/P ratio (0.06 for 0 bar CO to 0.30 for 1.0 bar CO), since most of the olefins formed in the cracking reaction cannot be hydrogenated at the partially poisoned hydrogenation component. Due to the longer residence time (with rising CO partial pressure), short-chain olefins are subjected to an increased oligomerization and partly subsequent dehydrocyclization to aromatics, which leads to the observed increment in C_{5+} selectivity with a simultaneous decrease in C_3/C_4 selectivity.

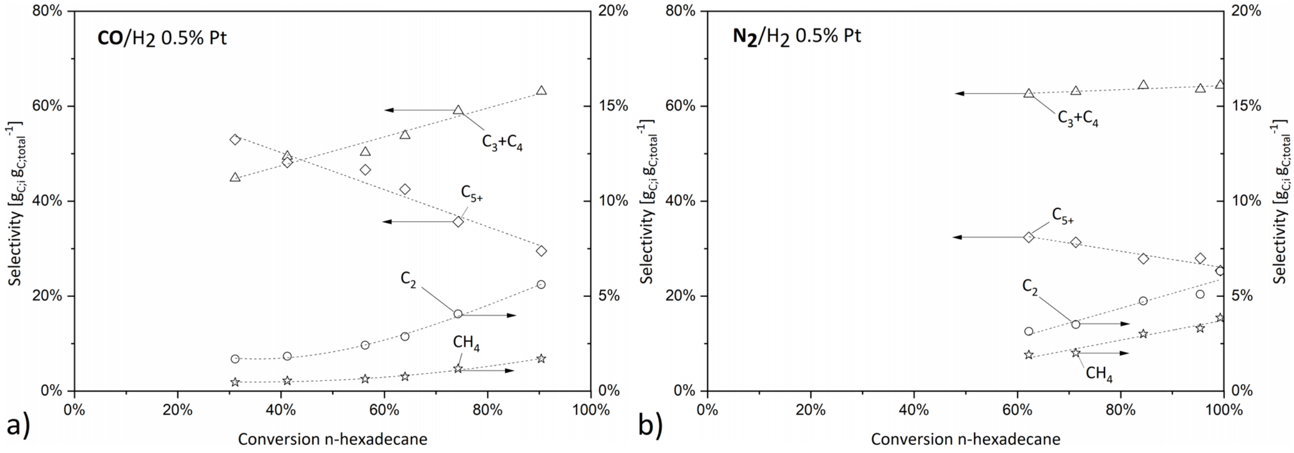


Figure 3. Influence of the conversion of *n*-hexadecane on the HC selectivities (a) for the cracking reaction with CO in the gas phase, (b) for experiments in which CO was substituted by N_2. The selectivities to methane and C_2-HCs are shown at the right ordinate and C_{3+} products on the left ordinate, respectively (for reaction conditions see Fig. 2).

Table 1. HC selectivities for a partial pressure of CO in a range of 0–6.5 bar (syngas conditions). Additionally, the modified residence time – adjusted by the change of total volume flow – to reach a constant *n*-hexadecane conversion of ≈55 % is listed (p_{total} = 20 bar, p_{H2} = 13 bar, $p_{n\text{-hexadecane}}$ = 0.5 bar, $m_{zeolite\ (H\text{-}ZSM\text{-}5,\ 0.5\ wt\,\%\ Pt)}$ = 0.97 g, T = 350 °C).

Partial pressure CO [bar]	Selectivity [wt_C %]				Modified residence time to reach a conversion of ca. 55 % [$kg_{zeolite}h\ m^{-3}$]
	CH_4	C_2	$C_3 + C_4$	C_{5+}	
0	2	3	63	32	0.43
1.0	2	6	58	34	0.57
2.5	2	6	58	34	0.65
3.5	2	4	55	39	0.85
4.5	2	4	57	37	0.85
6.5	2	3	53	42	0.95

3.2 Influence of Carbon Monoxide on the Cracking of *n*-Hexadecane as Model Substance (Zeolite without Pt)

To verify the theory of Pt poisoning by CO, additional experiments were carried out with an H-ZSM-5 zeolite without Pt as (de)hydrogenation component, as the Pt-free zeolite should perform the same way as the CO poisoned Pt/H-ZSM-5. Fig. 4 shows the *n*-hexadecane conversion and the O/P ratio at different modified residence times. For an easier comparison of the results, the data already depicted in Fig. 2 for the 0.5 wt % Pt zeolite in the presence of CO are displayed again. The cracking activity of both catalysts shows the same trend with increasing residence time. Also, the O/P ratio of the zeolite without Pt corresponds to that of the zeolite with Pt under syngas conditions, i.e., with CO. Deviations are attributed to the use of two different catalysts.

In the Supporting Information (Fig. S1), the HC distributions for both catalysts are shown as a function of conversion. Both catalysts exhibited the same selectivities, except slight differences with regard to C_1 and C_2 HCs. The catalyst with Pt has a slightly higher selectivity to methane and C_2 compounds probably due to hydrogenolysis or CO methanation at Pt sites.

3.3 Influence of H_2O on the Cracking of *n*-Hexadecane as Model Substance

During Fischer-Tropsch synthesis, water is always formed as a by-product of formation of HCs (mainly paraffins):

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow (-\mathrm{CH_2}-)_n + n\mathrm{H_2O} \tag{8}$$

By simultaneously evaporating water and *n*-hexadecane as model substances, the influence of water on hydrocracking on a zeolite loaded with 0.5 wt % Pt could be investigated. The H_2O partial pressure was increased up to 4.4 bar. The resulting HC selectivities for the cracking of *n*-hexadecane at different

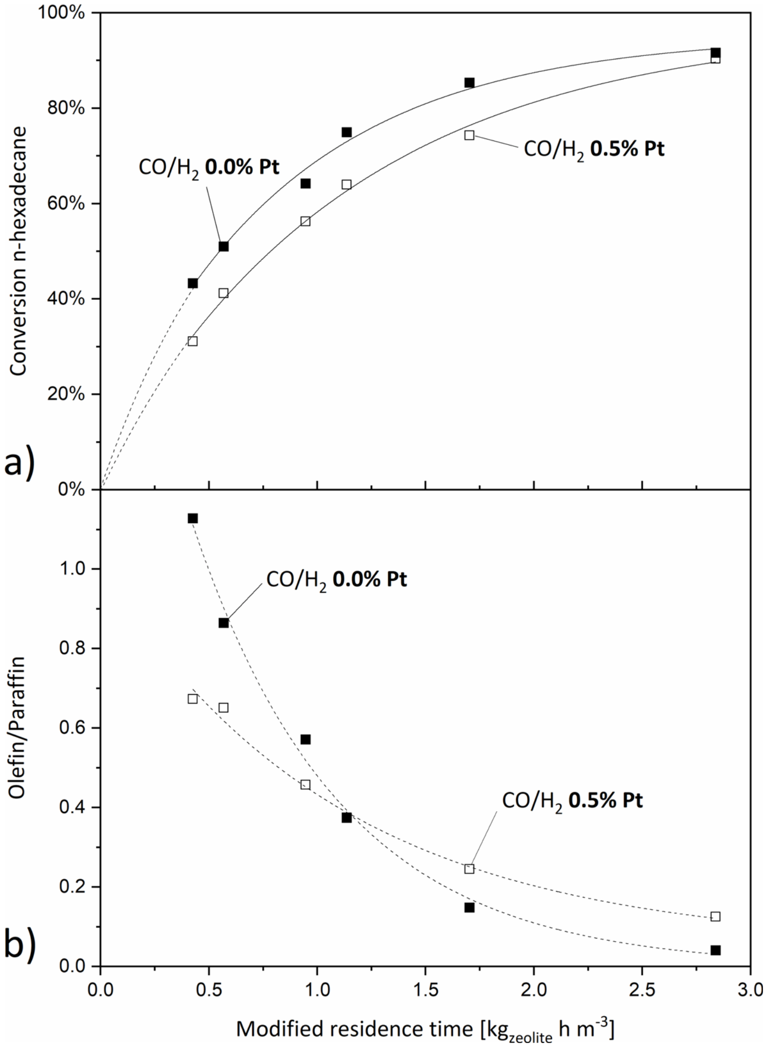


Figure 4. (a) Development of *n*-hexadecane conversion with increasing modified residence time for both catalysts (H-ZSM-5, 0.0 wt % Pt and H-ZSM-5, 0.5 wt % Pt) under the same reaction conditions. (b) Corresponding olefin/paraffin ratios. Note that the results for the catalyst containing 0.5 wt % Pt were already presented in Fig. 2 (p_{total} = 20 bar, p_{H2}/p_{CO} = 2, $p_{n\text{-hexadecane}}$ = 0.5 bar, $m_{zeolite}$ = 0.97 g, T = 350 °C).

conversions are presented in Tab. 2. As a reference, the HC selectivities for cracking of *n*-hexadecane without water in the simulated product gas of FTS are also displayed.

For the reference experiments (without water) a change in conversion was achieved by changing the modified residence time, whereas in the experiments with water the residence time was kept constant, which leads to a slight drop of conversion by the added water (59.4 % without H_2O and 49.6 % at 4.4 bar H_2O). Both series of experiments indicated that water has no effect on the selectivity (see Tab. 2). Hence, water only changes the activity of the hydrocracking catalyst to a minor extent, very probably due to competitive adsorption at the acid sites.

Similar results were found by Martínez et al. [35], who reported a strong decrease in conversion (relative 45 %) of *n*-hexadecane cracking on H-ZSM-5 (250 °C) after the addition of H_2O. Water molecules are expected to adsorb on the acidic sites of the zeolite and therefore compete with HC adsorption. However, Corma et al. [39] noticed by IR spectroscopy that this adsorption is only relevant at reaction temperatures below 350 °C. At temperatures higher than 400 °C, no interaction of water molecules with the acidic groups of the used USY zeolite has been observed. This could be the reason for the only slight decline in cracking activity after the addition of water observed in our experiments at 350 °C.

3.4 Reaction of Alcohols on Pt/H-ZSM-5 in Syngas Atmosphere or under Ideal Hydrocracking Conditions

In addition to aliphatic HCs, oxoproducts (i.e., mainly 1-alcohols) also occur as FT products. We already reported on the conversion of alcohols on the zeolite in a tandem FTS/cracking process, which took place at already low cracking temperature of only 210 °C [7]. The alcohols (about 10 wt$_C$ % of the HCs formed in FTS with a Co/Mn-FT catalyst) were completely converted to olefins or paraffins with the same carbon number [7]. Here, we investigated this in more detail by using *n*-butanol (C_4) as model substance. The corresponding HC distributions for the reaction of *n*-butanol are depicted in Fig. 5 with and without addition of carbon monoxide. Simplified illustrations of main reaction pathways alcohols undergo on the zeolite with and without CO in the feed gas are also presented and were deduced from the experimental results.

Under syngas conditions (Fig. 5a), i.e., with a feed gas containing CO, the presence of both longer C_{5+} and shorter C_{3-} compounds indicates simultaneous oligomerization and cracking. The reaction pathway involves dehydration of the alcohol to 1-butene, followed by further reactions such as oligomerization and dehydrocyclization to aromatics and subsequent cracking of the compounds formed. However, experiments without CO (Fig. 5b) show that CO partially poisons the (de)hydrogenation activity of Pt. As a consequence, the majority of the formed HCs (85 wt$_C$ %) are paraffinic C_4 HCs in case of absence of CO (Fig. 5b). Oligomerization and cracking then occurred only to a small extent. This indicates that in the absence of CO, the activity of Pt is not affected, meaning that *n*-butanol is rapidly dehydrated to 1-butene, which is then subsequently hydrogenated to *n*-butane and practically no oligomerization or cracking occur.

Table 2. Comparison of HC selectivities for cracking of *n*-hexadecane at different conversions for experiments with and without water (p_{total} = 20 bar, p_{H2}/p_{CO} = 2, $p_{n\text{-hexadecane}}$ = 0.5 bar, $m_{zeolite\ (H\text{-}ZSM\text{-}5,\ 0.5\ wt\%\ Pt)}$ = 0.97 g, T = 350 °C).

Conversion *n*-hexadecane [%]	Partial pressure H_2O [bar]	Selectivity [wt_C %]				Modified residence time [$kg_{zeolite} h\, m^{-3}$]
		CH_4	C_2	$C_3 + C_4$	C_{5+}	
CO/H₂						
90	0.0	2	5	63	30	2.84
74	0.0	1	4	59	36	1.70
64	0.0	1	3	54	42	1.14
56	0.0	1	2	50	47	0.95
41	0.0	1	2	49	48	0.57
31	0.0	0	2	45	53	0.43
CO/H₂ and H_2O						
59	0.0	1	3	54	42	1.07
55	1.3	0	2	52	46	1.07
52	2.9	0	2	47	51	1.07
50	4.4	0	2	49	49	1.07

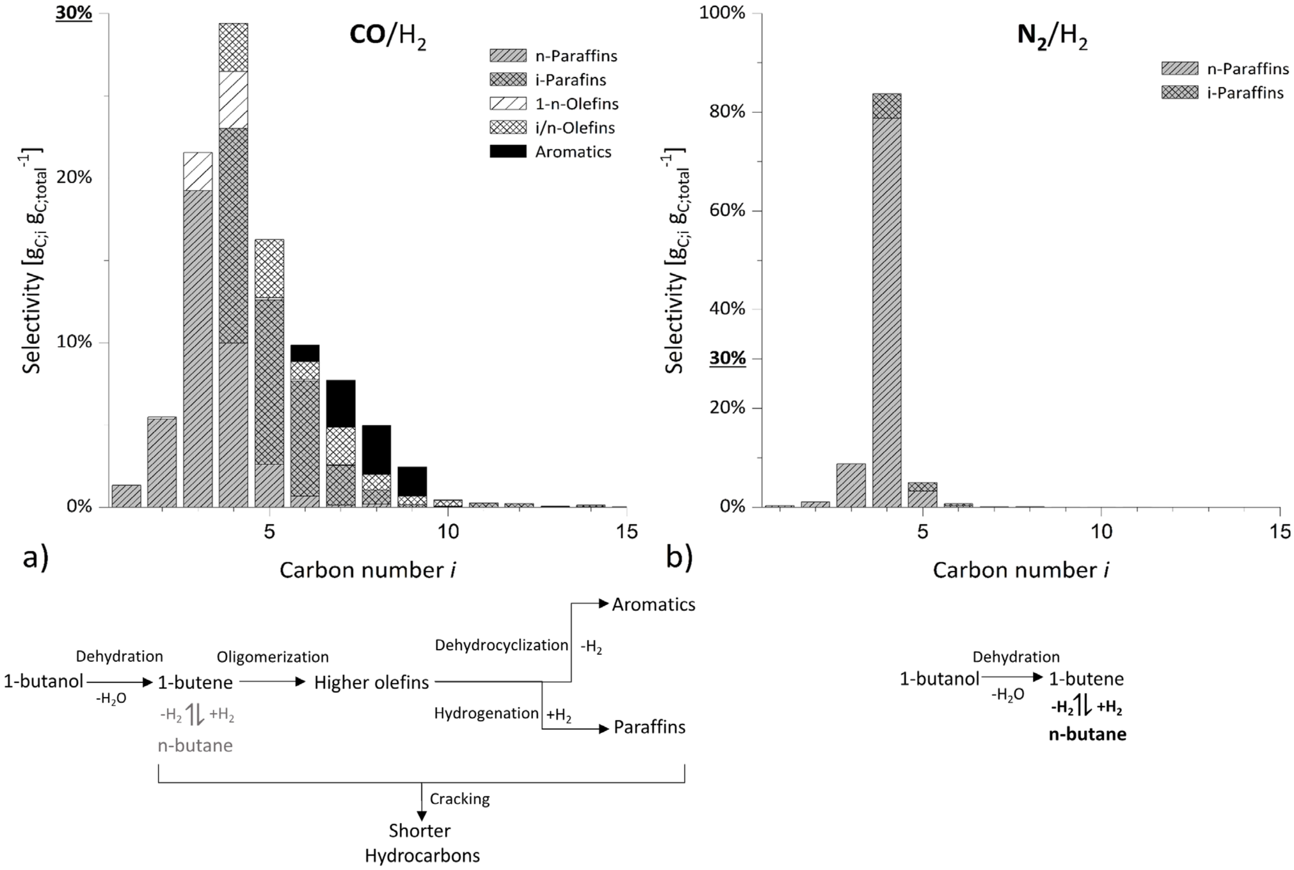


Figure 5. Comparison of HC distribution for the reaction of 1-butanol over H-ZSM-5 (a) in the presence of CO and (b) in the absence of CO. Also, the proposed simplified reaction schemes for the conversion of 1-butanol are illustrated. Faded text indicates a decreased (de)hydrogenation activity of the Pt sites (p_{total} = 20 bar, p_{H2}/p_{CO} = 2 (without N_2) or p_{H2}/p_{N2} = 2 (without CO), $p_{1\text{-butanol}}$ = 1.0 bar, $m_{zeolite\ (H\text{-}ZSM\text{-}5,\ 0.5\ wt\%\ Pt)}$ = 0.97 g, T = 350 °C, $X_{1\text{-butanol}}$ = 100 %, $\tau^*_{zeolite}$ = 1.08 $kg_{zeolite} h\, m^{-3}$).

3.5 Reaction of LPG Components as Model Substances on Pt/H-ZSM-5

Since the intention is here to maximize the selectivity of LPG in a tandem process of FTS and cracking, it was also investigated whether LPG compounds primarily formed by FTS undergo further reactions on the zeolite or not. During ideal bifunctional hydrocracking via β-scission of carbenium ions, the cracking rate of HCs $\leq C_5$ is very low. Thus, from a theoretical point of view, LPG components should therefore almost not react at the zeolite. To prove this assumption, the reaction of propene, propane, 1-butene, and *n*-butane as part of a simulated product gas of FTS was investigated separately.

Fig. 6 depicts the influence of the residence time on the conversion of these model HCs. With increasing residence time, an almost complete conversion of the olefins is finally reached. To the contrary, C_3 and C_4 paraffins were only converted to a much smaller extent. The olefins were hydrogenated to a certain extent on the zeolite (max. 35 % for propene, see Fig. S2), but oligomerization and cracking reactions also took place (see Fig. 7). Oligomerization of short-chain olefins on H-ZSM-5 was observed by various groups [40–42].

Paraffins were almost not dehydrogenated at all, due to the high equilibrium concentration at 350 °C and a high partial pressure of hydrogen. The much lower conversion of the paraffins can be explained on the one hand by the fact that dehydrogenation does not take place, and on the other hand that direct protonation of paraffins to carbocations is, in contrast to the protonation of the olefins, less favored.

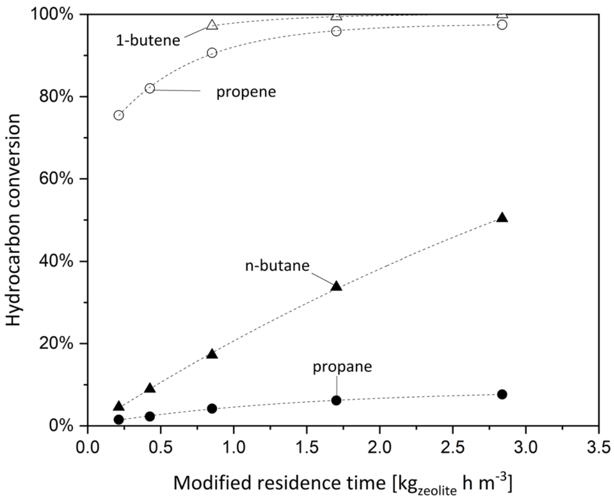


Figure 6. Evolution of the conversion of 1-butene, *n*-butane, propene, and propane with increasing modified residence time (p_{total} = 20 bar, p_{H2}/p_{CO} = 2, $m_{zeolite\,(H\text{-}ZSM\text{-}5,\,0.5\,wt\,\%\,Pt)}$ = 0.97 g, T = 350 °C, p_{HCs} = 1.0 bar).

3.5.1 Reaction of Propane and Propene under Syngas Conditions or Typical Hydrocracking Conditions on Pt/H-ZSM-5

Fig. 7a presents the HC selectivities for the conversion of propene with increasing residence time and thus also increasing conversion. As already mentioned, a maximum of 35 % of the converted propene is hydrogenated, and much more of the converted propene is oligomerized and cracked which is reflected in compounds $\geq C_4$ and $\leq C_2$. Since not only products with a carbon number that is an integer multiple of C_3 (i = $n \times 3$) are present, also cracking of theses oligomerized products takes place. For a detailed product distribution see

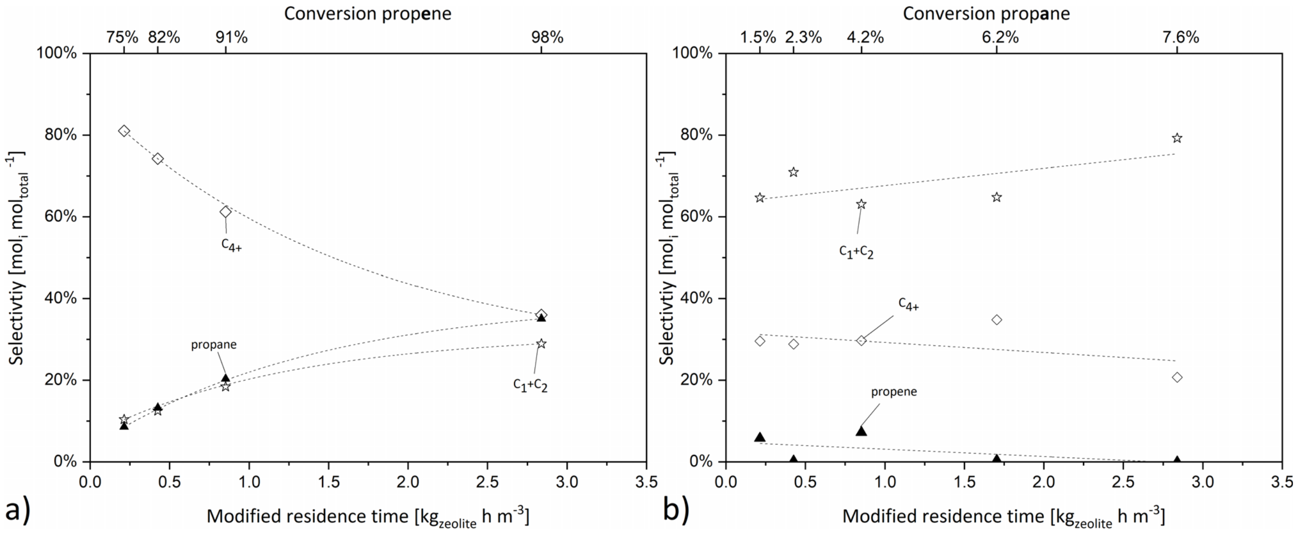


Figure 7. Evolution of the HC selectivities with increasing modified residence time for (a) propene as reactant and (b) propane, respectively. The corresponding conversions of the used HCs are indicated on the upper nonlinear abscissa (p_{total} = 20 bar, p_{H2}/p_{CO} = 2, $m_{zeolite\,(H\text{-}ZSM\text{-}5,\,0.5\,wt\,\%\,Pt)}$ = 0.97 g, T = 350 °C, p_{HCs} = 1.0 bar).

Fig. S3. An increasing residence time leads to more direct hydrogenation of propene to propane and also to an increase in Haag-Dessau cracking (more C_1 and C_2).

Fig. 7b demonstrates the HC selectivities for the conversion of propane as model substance. Even at a high residence time, where propene is almost completely converted (see Fig. 7a), only a very small fraction of propane (max. 8 %) is converted. The majority of reaction products are methane and C_2 compounds originating from Haag-Dessau cracking. Almost no dehydrogenation took place, which means that no propene is formed and available for oligomerization reactions.

In addition to the experiments under syngas atmosphere, "ideal" hydrocracking conditions (only H_2 and no CO in feed gas) were adjusted for the investigation of hydrocracking of propene and propane. Fig. S4 depicts the respective HC distributions without and for comparison with CO. In the absence of CO, propene is almost completely hydrogenated to propane and oligomerization is suppressed. Propane shows no change in reactivity in the presence of CO.

3.5.2 Reaction of *n*-Butane and 1-Butene under Syngas Conditions on Pt/H-ZSM-5

Besides C_3 components, also *n*-butane and 1-butene (C_4 components) were used as model substances for LPG components. The product selectivities with increasing modified residence time are given in Fig. 8. 1-Butene showed a high reactivity and was completely converted on the zeolite. With increasing residence time, the proportion of short-chain compounds (C_1 to C_3) increases due to Haag-Dessau cracking (C_1–C_2) and β-scission reactions (C_3). The proportion of chain-extended C_{5+} products decreased with longer residence time, respectively. If *n*-butane is used (Fig. 8b), mainly short-chain products are formed by cracking reactions, and the selectivity to long-chain compounds is very low since almost no oligomerization is taking place.

4 Conclusions

In an FTS/hydrocracking tandem process, the gas composition of FTS can influence the downstream cracking process. In this work, the product gas of the FTS was simulated by a respective gas mixture consisting of HCs, H_2, CO, and H_2O to investigate the influence of unreacted CO and of the FTS by-product H_2O on the cracking of *n*-hexadecane used as model hydrocarbon. The reaction of LPG components and alcohols, typically formed in FTS, on the hydrocracking catalyst (zeolite with Pt) was also examined.

The hydrocracking of *n*-hexadecane on Pt/H-ZSM-5 is influenced by the presence of CO in the feed gas. CO decreases the cracking rate due to partial poisoning of the Pt (de)hydrogenation component, as it strongly adsorbs. The selectivity is only slightly affected. The addition of water lowers the reactivity of *n*-hexadecane slightly but has no influence on the selectivity. Alcohols used as model substances are completely converted on the zeolite even at low temperatures under syngas conditions (CO present). Respective simplified reaction pathways are proposed. Besides dehydration to olefins, the oligomerization of these products as well as hydrocracking takes place. In the absence of CO olefins originating from dehydration of alcohols are immediately hydrogenated and no further reactions take place.

All tested LPG components showed a certain reactivity on the zeolite. Propene and 1-butene are almost completely converted by oligomerization, cracking, and to a certain extent also by hydrogenation. Propane and *n*-butane show reduced reactivity on the zeolite since the activation by direct protonation, needed to undergo further reactions, is less favored.

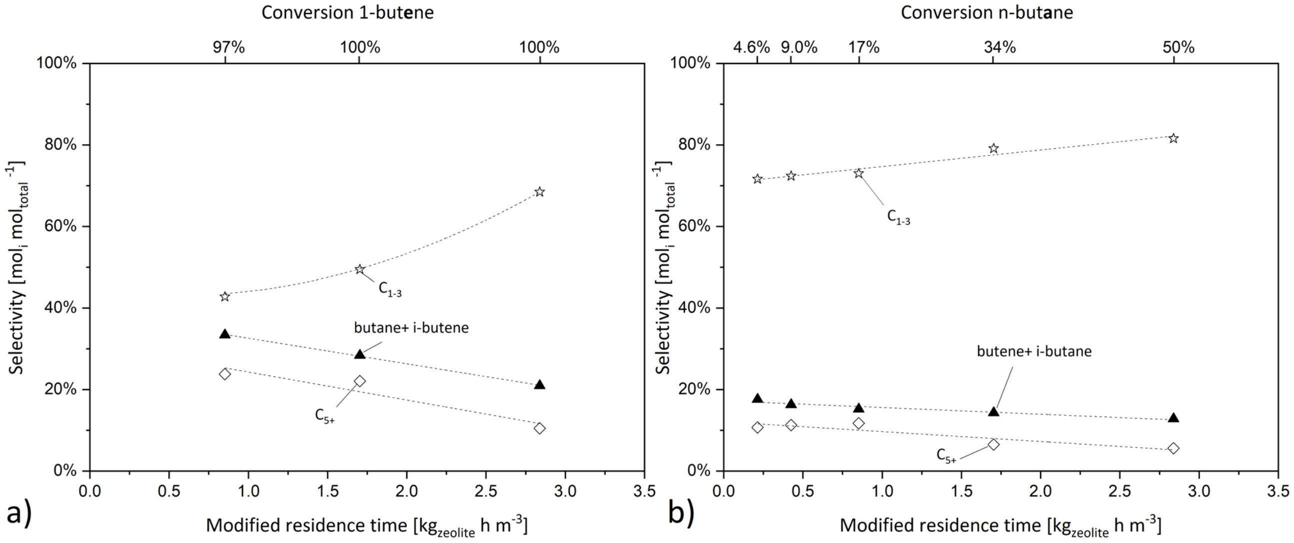


Figure 8. Evolution of the HC selectivities with increasing modified residence time for (a) 1-butene and (b) *n*-butane as reactant, respectively. The corresponding conversion of each C_4-HC is presented on the upper abscissa (p_{total} = 20 bar, p_{H2}/p_{CO} = 2, $m_{zeolite\ (H\text{-}ZSM\text{-}5,\ 0.5\ wt\ \%\ Pt)}$ = 0.97 g, T = 350 °C, p_{HCs} = 1.0 bar).

The results indicated that under certain circumstances it is beneficial to perform cracking of long-chain HCs (C_{5+}) not in a tandem process, but in a separate process after downstream FT product separation:

- CO decreases the activity of the used zeolite by partial poisoning of the Pt sites and, therefore, lowers the conversion at the same cracking severity compared to a "normal" hydrocracking process.
- The FTS by-product water also reduces the cracking activity.
- The tested LPG components, typically formed in FTS, showed reactivity on the zeolite.

Since the presence of CO as well as water negatively affects the cracking activity of the zeolite, but not the selectivity, a tandem process without product separation could still be carried out with the same outcome just at a higher cracking severity. On the one hand, this would lead to energy savings, since no product separation is necessary, but on the other hand this advantage could be outweighed by the thereby higher necessary cracking severity. The process separation would also require the additional provision of a clean hydrogen stream for the separated hydrocracking step. Since the syngas needed for FTS is produced by the use of green hydrogen from water electrolysis, the provision of the additional pure hydrogen stream would not pose a problem in a separated process. More importantly, as the LPG components (also part of the FT products) react on the zeolite and were partly converted to undesired C_1 and C_2 compounds, the implementation of a separated process could therefore increase the overall LPG yield.

In the light of these circumstances, a product separation upstream of hydrocracking after FTS can be considered as useful. Further studies are now conducted to evaluate the influence of CO on alternative metals such as Pd, since higher CO tolerances are reported.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/ceat.202300203. This section includes additional references to primary literature relevant for this research [43, 44].

Acknowledgment

The authors thank the Oberfrankenstiftung 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
D_{50}	[m]	mass median diameter
m	[kg]	mass
$\dot{m}$	[kg s^{-1}]	mass flow
$\dot{n}$	[mol s^{-1}]	molar flow
p	[bar]	pressure
S	[–]	selectivity
T	[°C]	temperature
V	[m^3]	volume
$\dot{V}$	[m^{3}s^{-1}]	volume flow
X	[–]	conversion

Greek letters

α	[–]	chain growth probability factor
β	[–]	beta position
τ^*	[kg$_{\text{zeolite}}$h m^{-3}]	modified residence time

Sub- and superscripts

C	carbon
i	compound

Abbreviations

ASF	Anderson-Schulz-Flory
FTS	Fischer-Tropsch synthesis
GC	gas chromatography
HCs	hydrocarbons
HPLC	high-performance liquid chromatography
H-ZSM-5	zeolite socony mobil-5 (hydrogen form)
LPG	liquefied petroleum gas
O	olefins
P	paraffins
TPD	temperature-programmed desorption

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