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On the effect of water during Fischer–Tropsch synthesis with a ruthenium catalyst

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Abstract

The addition of water during Fischer–Tropsch synthesis over a supported ruthenium catalyst led to a significant increase in product formation rates and significant changes in product selectivity, in particular lower methane selectivity and improved chain growth. Upon increasing water partial pressures, the total product distribution shifted from ASF distributions, with typical deviations due to olefin reinsertion, to a much narrower distributions. Such distributions can mechanistically not be explained by sole C_1-wise chain growth. An additional product formation route considering combination of adjacent alkyl chains to form paraffins ("reverse hydrogenolysis") has been proposed. The findings are discussed with regard to the crucial mechanistic role of water as a moderator in the kinetic regime of the Fischer–Tropsch synthesis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Ruthenium; Water partial pressure; Activity; Selectivity; Methane

1. Introduction

In the absence of the water gas shift reaction, water is the main product of Fischer–Tropsch CO-hydrogenation. Its presence can affect a catalyst's performance (activity and selectivity) in several ways. Whereas with iron-based catalyst studies dealing with the kinetics of syngas consumption generally show that the consumption rate decreases as water concentrations increase [1–6], the activity of cobalt catalysts has been reported to either be negligible [7–11], negative [12,13] or even positive [14–16]. The negative effects of water have been ascribed to the formation of inactive metal oxides (Fe: [1,3,10]; Co: [12,13]), in case of cobalt, where bulk oxidation appears thermodynamically not feasible, the observed catalyst deactivation was suggested to be caused by oxidation of highly dispersed phases or surface oxidation [12]. The underlying process responsible for the positive (autocatalytic) effect of water on the activity of cobalt catalysts remains unclear. Effects of facilitated intra-particle transport [16] as well as mechanistic aspects [17,18] have been considered.

Likewise, interesting are observations which show that product selectivity is almost not affected by water during FT-synthesis with iron [3,19,20], whereas with cobalt catalysts a significant product improvement (lower methane selectivity, higher chain growth probability, higher molar olefin contents, in particular α-olefins) has been reported [11,14,16,21,22]. These selectivity changes have been related to primary (chain growth) and secondary (olefin readsorption) reaction steps as affected by water [11,16,23,24].

The purpose of this study is to extend those experimental findings dealing with the impact of water and to better understand the mechanistic role of

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water by investigating the much less detailed studied FT-synthesis over ruthenium. Ruthenium is the metal most active for the FT-CO-hydrogenation [2]. At low temperature ($<150\,^{\circ}C$) and high synthesis gas pressures (>100 bar), it produces high molecular weight hydrocarbons ("polymethylene synthesis" [25,46]) indicating its ability to perform chain growth in its "cleanest" mode and it should, therefore, provide the simplest catalytic system of FT-synthesis, where mechanistic conclusions should be easiest [26]. With regard to the impact of water on the synthesis over ruthenium, it is known that ruthenium is active even if suspended in liquid water [27], indicating its resistance against oxidation. Later published kinetic rate equations indicate that water does indeed not affect the activity of ruthenium catalysts during FT-synthesis [2,9,28,34]. A positive effect of water on CO conversion over a TiO_2-supported ruthenium catalyst has however also been reported [14].

The majority of the few published studies dealing with product selectivity obtained during ruthenium catalysed FT-synthesis [9,29–34] show that rather typical FT-product distributions can be yielded at moderate reaction conditions (i.e. pressures ca. 1–20 bar, temperatures: 200–250 °C). From pulse studies with water co-feeding over supported ruthenium catalysts, Nijs and Jacobs [23] concluded that the presence of water promotes chain growth and they suggested a direct mechanistic involvement of water in the Fischer–Tropsch synthesis. A patent publication confirms improved C_{5+}-selectivity and reduced methane selectivity during FT-synthesis with water addition over a ruthenium catalyst in a fixed bed reactor [14]. With respect to the linkage between secondary olefin reactions and their possible impact on the total product distribution, ruthenium and cobalt seem to behave mechanistically similarly [9]. This includes the important effect of water on the extent and selectivity of secondary olefin reactions. These studies, all of which were carried out in fixed bed reactors, also indicate the difficulty of extraction kinetic information from experiments in a reactor system with concentration profiles. A systematic study dealing with the impact of water partial pressure on steady-state activity and selectivity during Fischer–Tropsch synthesis over ruthenium is however not available in literature. Our experiments were conducted in a continuously operated stirred slurry reactor, which allows for kinetic studies with variation of one single reaction parameter (i.e. water in this study) and therefore more straightforward interpretations of results obtained.

2. Experimental

The ruthenium catalyst was prepared by means of incipient wetness impregnation of a $RuCl_3{\cdot}xH_2O$ (p.a., Aldrich Chemicals) solution onto a silica gel support (Davisil^{TM}, grade 646, $d_{\mathrm{pore,avg}} = 150\,\text{Å}$). The final composition in mass ratios was 5 g Ru/95 g SiO_2. The catalyst pre-treated in a separate fixed bed reactor (calcination in nitrogen: temperature programmed (4 °C/min) from 30 to 200 °C (kept for 4 h), SV = 120 ml(NTP)/min/g_{Ru}; reduction in hydrogen: temperature programmed (4 °C/min) from 30 to 300 °C (kept for 4 h), SV = 120 ml(NTP)/min/g_{Ru}). An equivalent of 0.5 g ruthenium of the completely reduced catalyst ($d_{\mathrm{particle}} < 100\,\mu m$) was transferred under inert atmosphere to the autoclave reactor and suspended in ca. 450 ml squalane, the starting solvent. Fig. 1 shows a simplified flow scheme of the reactor set-up (reactor volume: 600 ml).

After a period of initial catalyst deactivation steady-state activity at a desired base case condition at very low conversion levels (i.e. $p_{H_2O} = 0.2$ bar, $T = 200\,^{\circ}C$, $p_{\mathrm{total}} = 15$ bar, $H_2/CO=2$ mol/mol), the water partial pressure was increased stepwise by addition of water via a temperature controlled saturator, whilst keeping the partial pressures of H_2 and CO constant. The reaction conditions are listed in Table 1. This experimental approach, which was successfully applied by Schulz et al. [11], allows for simulating higher conversions without changing the average reactor residence time (see Table 1). Total pressures, which were controlled with a pressure controlled argon flow added to the hot gaseous product stream after the wax trap and before the restricting needle valve, had to be varied according to the amount of water added. Each set of reaction conditions was held for at least 48 h and checked for steady-state conversion and selectivity. The base case experiment as well as other reaction conditions were repeated throughout the study to ensure for reproducibility.

Product analyses were performed off-line using the ampoule sampling technique [33] and gas chromatographs adapted to this technique [18,35]. Organic

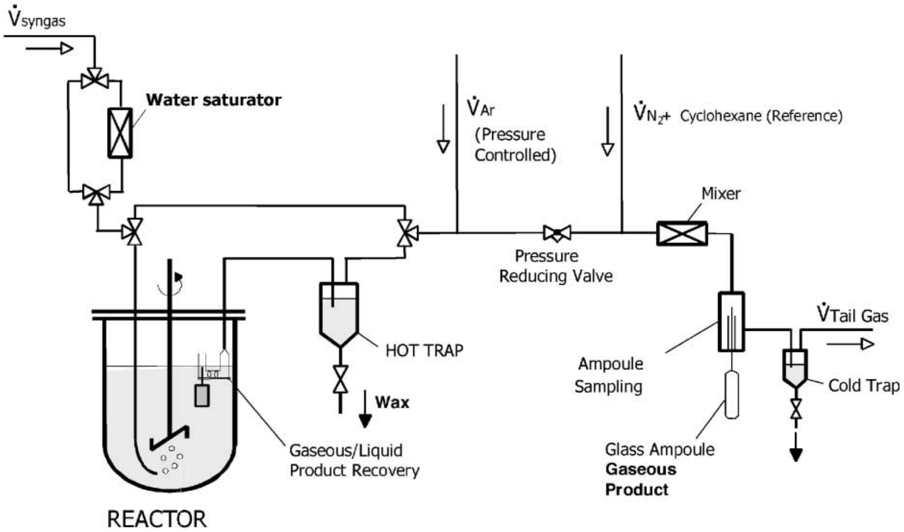

Fig. 1. Simplified flow scheme experimental set-up with a stirred slurry reactor.

compounds, which were volatile at reaction conditions (range C_1 to ca. C_{20}) were separated with a capillary column (OV-1 type, 50 m × 0.25 mm, 0.4 μm film) applying a temperature programme and detected with a flame ionisation detector (Gas Chromatograph Varian 3400). Inorganic compounds were separated on a packed column (Carbosieve) and detected with a thermal conductivity detector (gas chromatograph Varian 3300). Degrees of conversion and formation rates of organic compounds were directly calculated from the chromatograms by referring to the peaks of reference compounds (nitrogen and cyclo-hexane), which had been added to the product stream after pressure reduction.

Table 1
Reaction conditions of Fischer–Tropsch synthesis in a stirred slurry reactor[a]

	Base case	Water addition			Base case repeat
p_{H_2O} (bar)	0.17	1.27	2.37	4.54	0.16
p_{H_2} (bar)	9.8	9.7	9.6	9.5	9.8
p_{CO} (bar)	4.9	4.9	4.8	4.8	4.9
p_{CO_2} (bar)	–	–	–	–	–
p_{total} (bar)	15.0	16.1	17.1	19.0	15.2
$\tau_{gas,avg}{}^{b}$ (min)	17.5	17.7	17.9	18.3	17.4
$X_{CO,sim}{}^{c}$ (%)	(3.7)	20.8	33.0	48.9	(3.3)

[a] Catalyst: 5 g Ru/95 g SiO_2 (mass ratio), $d_{particle} < 100\,\mu m$, reaction temperature: 200 °C, space velocity ($H_2 + CO$) = 120 ml (NTP)/min/g_{Ru}, $(H_2/CO)_{feed} = 2$ mol/mol.

[b] Average residence time in reactor gas phase.

[c] Through water addition simulated CO conversion, calculated assuming: no CO_2 formation, no volume reduction.

3. Results

3.1. Rate of CO-consumption

Since no CO_2 was formed at detectable concentrations, the rate of CO-consumption equals the total formation rate of Fischer–Tropsch products on a carbon basis. This activity or the actual CO conversion increased markedly (ca. 3-fold) as the water partial pressure was increased from virtually zero to ca. 4.5 bar (see Fig. 2). This effect was completely reversible upon removal of water added to the feed, indicating the absence of severe catalyst deactivation during the series of experiments.

3.2. Methane selectivity/C_{5+}-selectivity

Methane is the thermodynamically most stable product of the Fischer–Tropsch CO-hydrogenation. Under typical Fischer–Tropsch conditions, its formation is however kinetically inhibited. At the base case

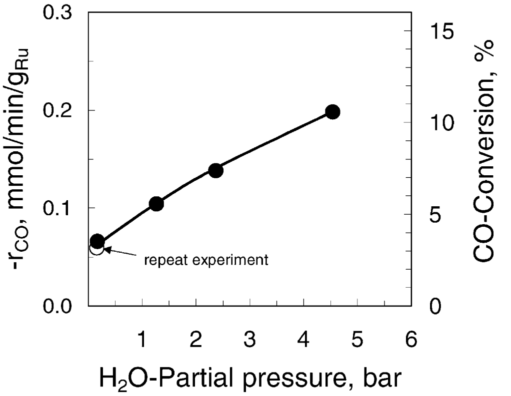

Fig. 2. Rate of CO-consumption ($-r_{CO}$) and CO conversion as a function of water partial pressure (reaction conditions, see Table 1).

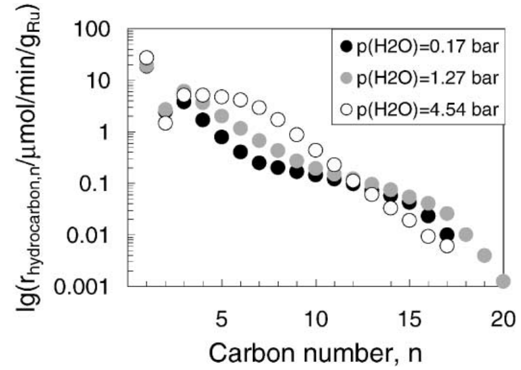

Fig. 4. Anderson–Schulz–Flory plots: molar product formation rates (hydrocarbons) obtained at different water partial pressures (reaction conditions, see Table 1).

condition at very low water partial pressure, a fairly high methane selectivity of nearly 30 C-% was found in the product. With increasing water partial pressures or at higher simulated conversion levels, a dramatic decline of the methane selectivity was obtained (see Fig. 3). This effect, which was also obtained with different cobalt catalysts [11,14,15,21,23] and with ruthenium (pulse test studies by Nijs and Jacobs [23]) underlines the crucial role of water inhibiting product desorption and therefore promoting chain growth [11].

As expected, C_{5+}-selectivity, which is often taken as a measure for the formation of valuable (i.e. non-gaseous) hydrocarbon products, shows an opposite trend (see Fig. 3), which is mainly due to the decreasing methane selectivity. A remarkable increase in C_{5+}-selectivity was obtained at the highest water partial pressure indicating a sudden drop in C_2–C_4 selectivity. These effects of selectivity were totally reversible as proven by repeating the base case.

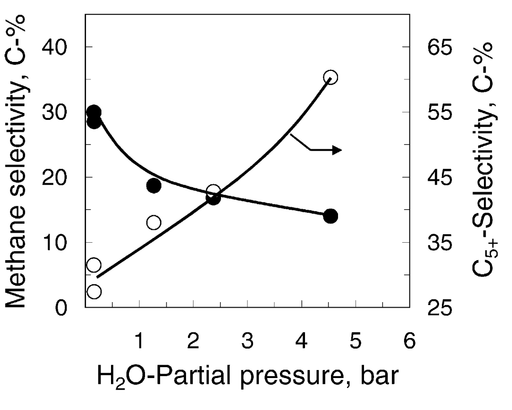

Fig. 3. Methane selectivity and C_{5+}-selectivity as a function of water partial pressure (reaction conditions, see Table 1).

3.3. Product distribution/chain growth

If the carbon chain is formed stepwise by insertion or addition of C_1 intermediates with constant growth probability, a straight line is observed in the so-called Anderson–Schulz–Flory diagram (semi-logarithmic plot of molar product contents vs carbon number), the slope of the line reflecting the chain growth probability α [1]. Fig. 4 shows the total molar product formation rates of the base case experiment and of experiments with water addition.

All distributions show pronounced deviations from ideal polymerisation kinetics. At low water partial pressures ($p_{H_2O} = 0.2$–2.4 bar), they show a kink at C_2 and a curvature (left-bend) with increasing carbon number, which end up in a straight line in the carbon number fraction C_{10}–C_{15} (note: the drop from ca. C_{15} onwards is due to the sampling method). These deviations are typically attributed to secondary reactions, i.e. chain length dependent reinsertion of primarily formed α-olefins[1] [9,24,36–40]. Judging from the slopes the chain growth probabilities at very low

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[1] Note: The incorporation of co-fed olefins during FT-synthesis with ruthenium has been proven by several authors (e.g. [9,30–32]) and was also proven to take place at the base case conditions in the present [43].

carbon numbers (C_3–C_7), which are hardly affected by secondary reactions, increase with increasing water partial pressure. This reflects a promoting effect of water on the primary chain growth probability.

As the water partial pressure was increased further, this distribution pattern shifts towards a differently shaped curve with almost similar molar formation rates of products in the range C_3–C_6 followed by a constant drop (straight line) at higher carbon numbers. This unusual and reproducible product distribution cannot be explained by C_1-wise chain growth and effects of secondary olefin reactions (see below).

3.4. Olefins

Linear α-olefins and paraffins are the main primary products of the Fischer–Tropsch CO-hydrogenation. α-Olefins can readsorb under reaction conditions and undergo secondary reactions, such as hydrogenation, double bond shift and act as chain starters (reinsertion) [9,38]. In the absence of these reactions, a chain length independent molar olefin selectivity of ca. 70–80 mol% is expected [38,41,47]. Fig. 5 depicts the molar olefin contents in the respective hydrocarbon fractions with the same carbon number as a function of carbon number as observed at the different water partial pressures.

These curves are characterised by deviations from primary selectivity: a low value at C_2, which reflects the high reactivity of ethylene, and—in particular at low water partial pressures—a decline with increasing carbon numbers from C_3 onwards, which is due to increasing residence times of longer chain products as a result of chain length dependent solubility [24,36–40,42] or diffusivity [9,16]. This decline is much less pronounced at higher water partial pressures. In fact, almost horizontal lines at ca. 20–35 mol% have been obtained here, which indicates the absence of secondary hydrogenation/reinsertion and should therefore reflect almost primary selectivity.

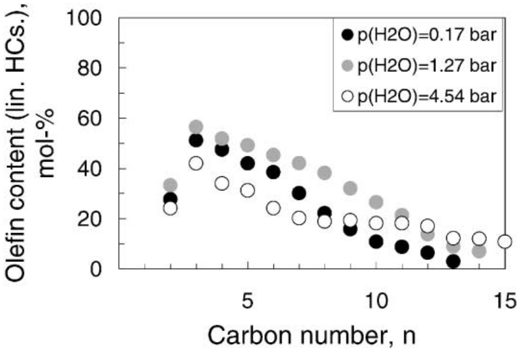

Fig. 5. Molar olefin content in the fraction of linear hydrocarbons with the same carbon number as a function of carbon number obtained at different water partial pressures (reaction conditions, see Table 1).

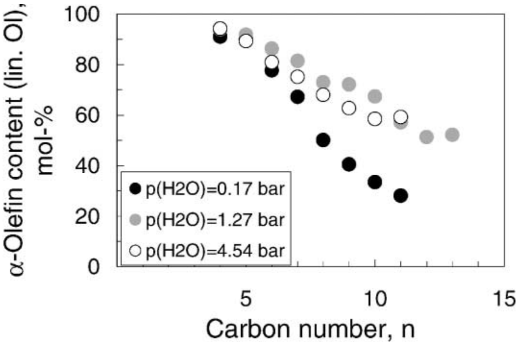

Fig. 6. Molar α-olefin content in the fraction of linear olefins with the same carbon number as a function of carbon number obtained at different water partial pressures (reaction conditions, see Table 1).

The extent of double bond shift isomerisation can easily be observed from the plot of α-olefin contents in the fraction of the linear olefins with the same carbon number as a function of carbon number (see Fig. 6). Assuming a primary α-olefin selectivity of 95–100 mol% [41,47] within these olefin fractions, the chain length dependent deviations observed at low water partial pressures indicate secondary double bond shift to occur and to be strongly inhibited by water. All these results were completely reversible/reproducible.

4. Discussion

The most striking results of this paper are the enhancement of catalyst activity and the Fischer–Tropsch untypical total product distribution at higher water partial pressures. The observed increases in reaction rate, C_{5+}-selectivity, chain growth probability and olefinicity and the decrease in methane selectivity are in accordance with results obtained with several cobalt catalysts [9,11,14,15,18,22] and a ruthenium catalyst [14].

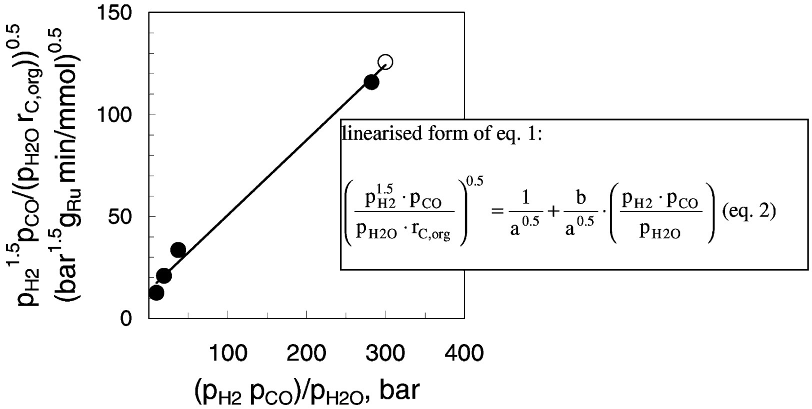

Fig. 7. Graphical test of the linearised form of the rate equation (Eq. (1)) (reaction conditions, see Table 1).

Iglesia [16] proposed the formation of a separate intra-pellet water or water-rich phase, which would facilitate CO and H_2 transport within the catalyst structure and, therefore, increase the accessibility of transport limited regions within porous pellets as a possible explanation for this ‘autocatalytic’ effect, which was only observed with larger pore support materials such as TiO_2 and large pore SiO_2. Here capillary effects, which lead to the formation of a separate condensed water phase would be ‘delayed’ until much higher water partial pressures; whereas in small pore supports, a water phase would even be formed at very low water partial pressures or low conversions. This would explain why water only affected the activity of cobalt supported on large pore material and why this effect ‘saturated’ at higher CO conversions. This effect of water on otherwise moderate to severe reactant transport limitations would also be responsible for the observed low methane selectivity and high olefin and C_{5+}-selectivity, since more pronounced concentration profiles of H_2 and CO along the catalyst pores would favour the formation of shorter hydrocarbons. The author, however, mentions that independent evidence for this proposal or alternate explanations for these effects of water would still be needed.

In this study, very small catalyst particles (diameters below 100 μm) have been used in order to ensure for absence of intra-pellet transport limitations—at least of the reactants. A rate enhancement due to the suggested moderation of transport effect [16] therefore appears unlikely. It can however not be excluded completely.

Schulz et al. [11] explained their findings on selectivity changes as observed upon variation of water partial pressure during FT-synthesis over a modified cobalt catalyst in a slurry reactor in terms of selective inhibition of individual reaction routes by water (e.g. inhibition of product desorption and olefin readsorption), without however making more detailed suggestions about the mechanistic occurrences involved.

A recently published rate equation [17,18], which is based on mechanistic assumptions,[2] predicts a positive effect of water at low syngas conversion levels. This rate equation, which reads as follows (Fig. 7)

$$r_{C,org}=\frac{ap_{CO}p_{H_2}^{1.5}/p_{H_2O}}{(1+bp_{CO}p_{H_2}/p_{H_2O})^2} \tag{1}$$

has been proven to predict rates of FT-synthesis with different iron- and cobalt-based catalyst over a broad range of experimental conditions as applied in slurry reactors very well [17,18,42]. Fig. 6 shows a reasonable fit ($R^2 = 0.99$) of this equation and the activity data obtained with the ruthenium catalyst of this study.

Mechanistically interpreted, an increase in water partial pressure would lead to a decrease in the surface concentration of carbon, which is thought to occupy

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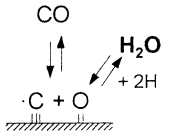
[2] Kinetically controlled polymerisation, irreversible hydrogenation of CH_x species, equilibria between surface species H, CO, C, O and OH, and H_2, CO and H_2O.

most of the catalyst surface [6,17,18] and to inhibit the Fischer–Tropsch reaction:



Besides this “cleaning” effect, water supplies a source of surface hydrogen, which is needed to form CH_2 and CH_3 and alkyl surface species leading to enhanced increase in CO-consumption. This increased availability of monomer species might also explain the experimentally observed increase in primary chain growth probability or C_{5+}-selectivity. Very high water partial pressures would result in a severe depletion of surface carbon and the rate would decrease again (see [17]).

The question of what might be the reason for the untypical total product distributions obtained at the higher water partial pressure in this study however still remains. A closer look at this distribution in comparison with the more typical base case product, in particular a look at the non-logarithmic weight distribution, reveals that the distribution yielded at the high H_2O partial pressure is considerably narrower, peaking at around C_6 (the C_1 concentration being an exception, see Fig. 8). As mentioned above, this distribution cannot be explained by secondary olefin reinsertion. Other olefin reactions—such as metathesis—can also be ruled out since the α-olefin distributions are as represented previously (see Section 3.3). Hydrogenolysis of the heavier products (at least of paraffin) appears also unlikely, because no fragments of squalane, which would easily have been identified in the product spectra, were detected. Since experimental artefacts or non-steady-state conditions can also be excluded, we propose that an additional product formation route might be the cause.

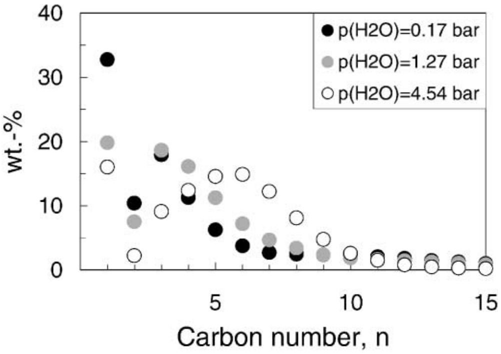
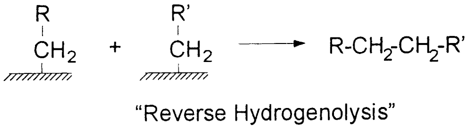


Fig. 8. Weight distribution of total product obtained at different water partial pressures (reaction conditions, see Table 1).

In the following we are considering termination reactions by random combination of two growing adjacent alkyl chains.[3] This scenario would be well in line with the interpretation of the rate and selectivity enhancing effect of water (see above), since there might exist a reaction condition at which the concentration of alkyl chains is fairly high and combination reaction to yield a linear paraffin becomes likely:



A modification of the ideal ASF model accounting for a random combination of growing alkyl chains has in fact already been developed by Novak et al. [45]. The weight distribution was expressed as follows:

$$W_n = \frac{n[\bar{\alpha}^{n-1} + 1/2\mu(1-\bar{\alpha})(n-1)\bar{\alpha}^{n-2}](1-\bar{\alpha})^2}{1+\mu} \tag{2}$$

with μ the ratio of termination by reverse hydrogenolysis rate constant k'_t to the Anderson–Schulz–Flory termination rate constant k_t:

$$\mu = \frac{k'_\mathrm{t}}{k_\mathrm{t}} \tag{3}$$

and the modified growth probability

$$\bar{\alpha} = \frac{k_\mathrm{p}}{k_\mathrm{p} + k_\mathrm{t} + k'_\mathrm{t}} = \frac{\alpha}{1+\mu(1-\alpha)} \tag{4}$$

(k_p, chain propagation rate constant; α, ASF chain growth probability).

To our knowledge, this equation has never been applied to fit experimental data. Applied on our data it does seem to reflect the right trend (see Fig. 9). The

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[3] Note: the assumption of a random combination seems to be justified looking at product distributions obtained in hydrogenolysis of paraffins over ruthenium catalysts [44].

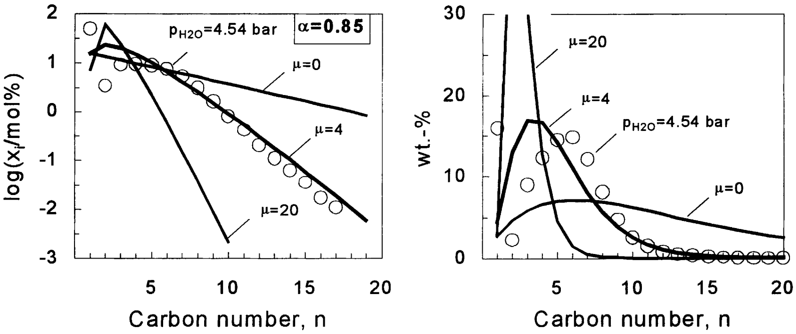

Fig. 9. Fitting of experimental data ($p_{H_2O} = 4.54\,\text{bar}$) using the reverse hydrogenolysis model [45]; variation of parameter $\mu = k_t'/k_t$ at $\alpha = 0.85$; left: ASF distributions; right: weight distribution of total product.

parameter $\bar{\alpha}$, which relates to an α value of 0.85 indicates a very high 'primary' chain growth probability. The parameter $\mu = 4$ reflects a preferred desorption route by alkyl–alkyl combination. This additional paraffin formation route would also result in lower primary olefin selectivity. This is in qualitative agreement with our experimental findings (see Section 3.3) indicating lower primary olefin selectivity at high H_2O partial pressures. This can be concluded, since the decrease in the olefin content as a function of carbon number becomes less with increasing p_{H_2O}. At high water partial pressure, a constant olefin content of ca. 20 mol% was obtained in the region of C_7–C_{12}.

Finally, it should be noted that there is no direct proof for the validity of the reverse hydrogenolysis model. The described proposal by Novak et al. [45] is not too good. A modified model incorporating carbon number dependency is currently being developed. A more exact match can be obtained with a Poisson distribution. This would mechanistically, however, not be plausible to the authors of this paper.

5. Summary

The addition of water during Fischer–Tropsch synthesis over a ruthenium led to an increase in catalyst activity and significant changes in product composition. Selectivity was affected positively, since methane formation was suppressed and chain growth enhanced. These effects and the presence of an unusual narrow product distribution might be a result of water indirectly affecting mechanistic occurrences on the catalyst surface such as 'surface cleaning' and providing a hydrogen source for the formation of chain growth monomers and alkyl surface species.

Yielding narrow product distributions in a one-stage process circumventing ASF restrictions may be of technical interest and might be incentive for further studies regarding the crucial effect of water in the kinetic Fischer–Tropsch system.

Acknowledgements

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