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Fischer-Tropsch synthesis over an alumina-supported cobalt catalyst in a fixed bed reactor – Effect of process parameters

Ljubiša Gavrilović [a,b,*], Erik A. Jørgensen [b,d], Umesh Pandey [b], Koteswara R. Putta [b], Kumar R. Rout [b,c], Erling Rytter [b,c], Magne Hillestad [b], Edd A. Blekkan [b]

[a] Institute for Energy Technology (IFE), P.O. Box 40, No-2027, Kjeller, Norway
[b] Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Sælands vei 4, 7491, Trondheim, Norway
[c] SINTEF Industry, NO-7465, Trondheim, Norway
[d] Rosenberg Worley, Bangarvågsgata 15, 4077 Hundvåg, Norway

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ABSTRACT

Fischer-Tropsch synthesis has been investigated over a commercial type cobalt-based catalyst (20 %Co/0.5 %Re/γ-Al_2O_3) by varying the H_2/CO ratio (2.55–1.12), CO conversion (15–75 %), reaction temperature (210 °C, 230 °C), and by adding water to the syngas. The experiments were conducted in a fixed bed reactor with the main purpose of obtaining experimental data to be used in the development and fitting of a mechanistic model. A positive effect of water on the catalyst activity was found for experiments with a H_2/CO ratio higher than 1.7. Water was found to always increase the C_{5+} selectivity regardless of the H_2/CO ratio. Increasing conversion led to increased C_{5+} selectivity. The selectivity to CO_2 was significantly enhanced at higher conversions (high water partial pressure), particularly with the lowest $H_2/CO = 1.12$, interpreted as the emergence of water-gas shift activity. Re-oxidation of cobalt, probably limited to small cobalt particles, is proposed as the main deactivation mechanism caused by water while a steeper deactivation curve was found for higher temperature, indicating that sintering also may play a role.

1. Introduction

Fischer-Tropsch synthesis converts synthesis gas (H_2 + CO) into a wide range of hydrocarbons that can be refined into drop-in commercial products like diesel and jet fuel [1]. Syngas may be derived from natural gas, coal, and biomass. The related processes are called GTL (gas-to-liquids), CTL (coal-to-liquids) or BTL (biomass-to-liquids) [2]. The ratio between hydrogen and carbon monoxide and the impurity content in the syngas can differ depending on which feedstock is used. In the case of coal or biomass, it also depends on the gasification technology [3]. While the CTL and GTL processes are established commercial technologies, the BTL process is still challenging concerning the scale and complexity of the process, questioning the economic feasibility [4]. However, liquid fuels produced via the Fischer-Tropsch process from biomass-derived syngas promises an attractive, clean, carbon-neutral and sustainable energy source [5]. The possibility to work with the existing fuel infrastructure and versatility in feedstock and products are key advantages of using the BTL-FTS process route. Another benefit is the ability to utilize the whole organic biomass matter. Biomass represents the only practical renewable source of carbon, necessary for the production of liquid hydrocarbon fuels and chemicals [6].

Fischer-Tropsch synthesis on cobalt catalysts have been subject to thorough investigations since the development by Fischer and co-workers in the 1920s–1930s [7]. Cobalt-based catalysts are of particular interest for industrial applications due to high activity at low temperatures, high selectivity towards long-chained hydrocarbons and a long life-time [8]. A lower deactivation rate is usually found using Co catalyst under pure synthesis gas [9], but Co is more sensitive to impurities when compared to iron-based catalysts, the major alternative [10]. Cobalt catalysts are often considered to have a negligible or low activity for the WGS (water gas shift) reaction compared to iron [11], making it suitable for applications using hydrogen-rich synthesis gas. Biomass gasification results in low $H_2/CO = 1$, thus, the installation of a WGS reactor prior to the FT reactor in order to adjust the ratio is usually proposed. It has, however, been observed that Co catalysts might develop WGS activity at high CO conversion levels depending on the H_2O/H_2 ratio level [12]. Addition of promotors (e.g. Re, Ru, Pt) mainly enhances catalyst reducibility and increases Co dispersion [13]. A

* Corresponding author.
E-mail address: ljubisa.gavrilovic@ife.no (L. Gavrilović).

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positive correlation with Co activity and selectivity was also reported upon Re promotion [14–16].

In order to do a good and realistic design of a potential BTL plant, it is necessary to have a kinetic model that captures major variations of reaction rates and selectivities subject to changes in process parameters. To reduce the investment and the operational costs and to efficiently use the syngas in a once-through concept, it is beneficial to operate at high CO conversion levels. Thus, it is essential to understand the catalyst behavior at high CO conversion levels with different H_2/CO ratios. The selectivity towards heavier hydrocarbons depends on process conditions like temperature, pressure, H_2/CO ratio and water partial pressure. Therefore, a suitable model should include these variables. It is also important to understand the effect of process parameters on the selectivity, thus the model should include a description of the rates of formation of the various products (chain growth model). It is established that oxidation of bulk cobalt metal does not occur under typical FTS conditions, however, small cobalt metal particle properties may differ considerably from those of the bulk metal. Thus, re-oxidation of a fraction of the metal in a cobalt catalyst caused by the indigenous water during FTS might be thermodynamically feasible [17].

The objective of this work is to investigate the effects of process conditions such as H_2/CO ratio (2.5−1.0), CO conversion level (15–75%), added water in the syngas, and temperature (230 °C, 210 °C) on activity and selectivity of a commercial type cobalt-based Fischer-Tropsch catalyst. The experiments aim to provide a detailed kinetic study which can be used in developing a kinetic model covering all important aspects. Developing new concepts with the aim of process intensification could be particularly relevant for FT-BTL plants that due to feedstock logistics cannot be of the mega-scale typically applied for plants using fossil-based feedstocks.

2. Experimental

Fischer−Tropsch synthesis experiments were performed with different H_2/CO ratios at high CO conversions over a commercial type 20 %Co/0.5Re ɣ-Al_2O_3 catalyst in a stainless steel fixed-bed reactor at different temperatures (210 °C and 230 °C) and 20 bar. A detailed description of the experimental setup can be found elsewhere [13]. The catalyst was provided by Equinor. The feed gas compositions were H_2/CO = 1.12, 1.41, 1.72, 2.13 and 2.55, with corresponding catalyst loadings m_{cat} = 4.0 g/1.5 g, 1.85 g/0.5 g, 1.5 g/0.6 g, 1.0 g/0.3 g, and 0.9 g/0.35 g for temperatures 210 °C/230 °C, respectively. The catalyst mass was different in order to achieve comparable conversion levels. Additional water was in some cases added to the syngas with the purpose of simulating high conversion levels. Different CO conversion levels were obtained by changing the syngas flow, typically every 24 h in order to record a steady state behavior of the catalyst before changing the conditions. A simple formula was used when changing the conversion:

$$F_{new} = \frac{F_{old} * X_{old}}{X_{new}}$$

Where F_{old} is the old flow, X_{old} is the old conversion, X_{new} is desired conversion and F_{new} is the new flow required to reach desired conversion. In most cases the flow needed to be adjusted few times in order to reach desired conversion of 50 or 70 %. This was especially difficult with the low H_2/CO ratios, particularly for reaching higher conversions. All the experiments were performed as follows:

1 Initial conditions: syngas flow of 250 mL/min.
2 Syngas flow adjusted to obtain 50 % conversion.
3 Syngas flow adjusted to obtain 70 % conversion.
4 Syngas flow adjusted back to initial conditions (250 mL/min syngas).
5 Keeping the initial conditions, increase the total pressure to 22 bar and add water corresponding to 2 bar water partial pressure to the syngas flow.

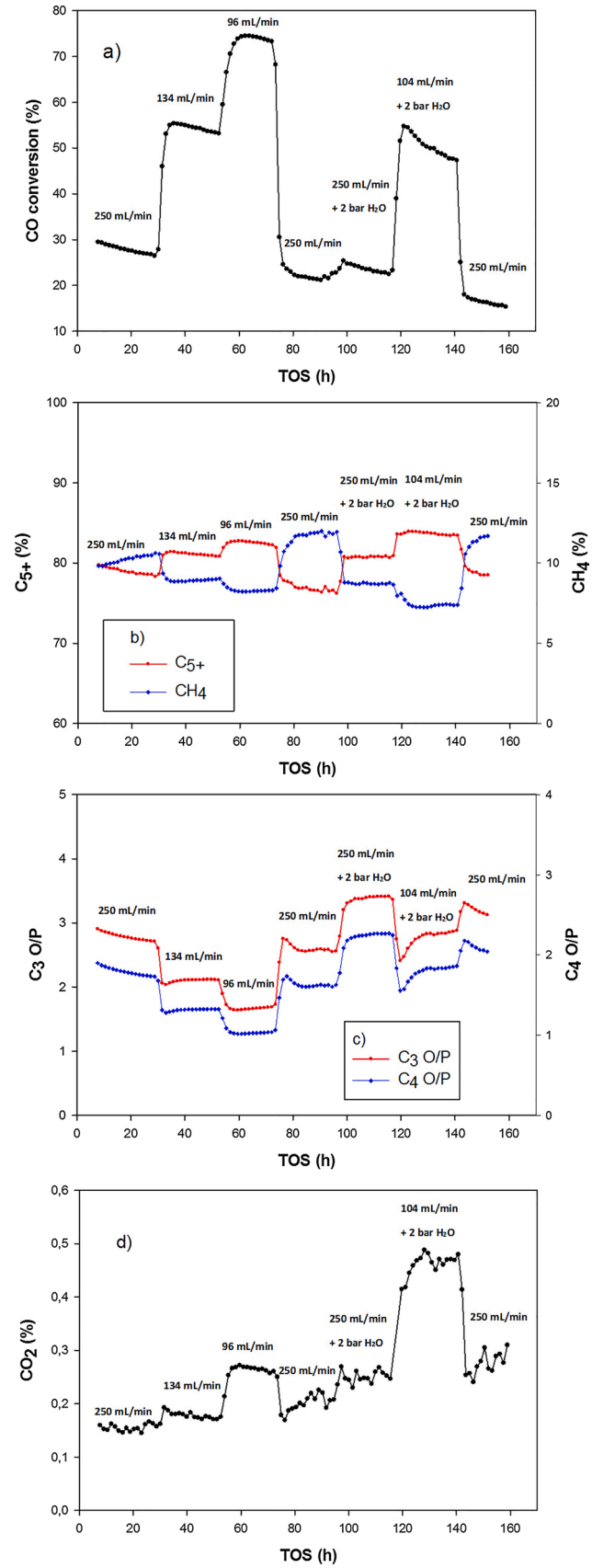

Fig. 1. Catalytic results at different conditions vs Time on Stream (TOS) with H_2/CO = 2.13 at 210 °C and 20 bar. a) CO conversion b) Selectivitites to C_{5+} and CH_4 c) Olefins to paraffins ratio for C_3 and C_4 hydrocarbons d) Selectivity to CO_2.

6 Syngas flow adjusted to obtain 50 % conversion, and the water flow rate adjusted correspondingly to keep 2 bar water in the feed.
7 Syngas flow adjusted back to initial conditions (250 mL/min syngas), the total pressure decreased to 20 bar and the water flow stopped.

After every ~24 h time on stream (TOS) activity data, reported as Site Time Yield (STY), were collected based on steady-state measurements at the corresponding conditions. Selectivity data are reported from the same analysis points, typically at comparable CO and constant conversions, based on the analysis of CO, N_2 (internal standard), CO_2 and C_1–C_4 hydrocarbons in the gas phase. Since the focus is on the amount of higher hydrocarbons, the selectivity is reported in the usual way as C_{5+} and CH_4 selectivity, and in addition the selectivity to CO_2 is reported.

The standard catalyst characterization techniques (H_2 - chemisorption, N_2 physisorption measurements and TPR - temperature programmed reduction) were performed in order to determine dispersion, surface area, pore size, pore volume and reduction profile of the commercial type catalyst. A detailed description of the characterization techniques used can be found in our previous publications [10,18,19].

3. Results and discussion

3.1. Catalyst characterization

H_2 - chemisorption was performed in order to determine the Co dispersion. The resultant dispersion of 7 % was found which indicates an average cobalt particle size of ~13 nm assuming spherical particles. The commercial type catalyst exhibits a surface area of 131 m^2/g, an average pore diameter of 12.1 nm and a pore volume of 0.47 cm^3/g based on the BET and BJH method, respectively. These characterization results are in accordance with our previous publication where a similar Co-based catalyst was synthesized in-house [18]. The TPR experiments showed a typical profile usually found for cobalt supported on alumina, with two main peaks corresponding to a transition from Co_3O_4 to CoO (~300 °C) and from CoO to Co° (~400 °C). The result coincides well with findings in the literature [20].

3.2. Fischer-Tropsch synthesis

The effect of process parameters on activity and selectivity of the Co-based Fischer-Tropsch catalyst will be described in separate chapters as follows: effect of syngas flow, effect of feed gas composition, effect of temperature, effect of water. Finally, WGS activity and catalyst deactivation will also be discussed.

3.2.1. Effect of syngas flow

The evaluation of the experiment with $H_2/CO = 2.13$ at 210 °C with changes in CO conversion and water addition is shown in Fig. 1. a). Other H_2/CO ratios (Figs. S1–S4 in the supplementary information) followed the same trend. The same trend is also observed with experiments performed at 230 °C. The effect of temperature will be discussed in a separate chapter. The effect of conversion level on catalyst activity will be discussed together with the effect of H_2/CO ratio in the next chapter. The Fischer-Tropsch product selectivities are well-documented to be highly dependent on the conversion level [14,21]. For every H_2/CO ratio, we found that increasing conversion leads to increased selectivity to C_{5+}, CO_2 and decreased selectivity to methane and reduced olefin to paraffin ratio, Fig. 1. The last period showed higher C_{5+} selectivity when compared with the same periods with the constant flow (250 mL/min). This might be due to the small differences in conversion levels, but also due to changes of the catalyst during high conversions and water addition. Small Co surface particles, typically responsible for more methane and less C_{5+} selectivity, are probably re-oxidized and contribute less to the hydrocarbon distribution compared to larger particles which are responsible for higher C_{5+} selectivity. At the same time the formed cobalt oxide, probably CoO, can contribute to increased CO_2 selectivity in the last period, Fig. 1. d). When the syngas flow is reduced, the resulting longer residence time in the reactor gives a higher probability of secondary reactions taking place. This results in higher chain-growth probability and enhanced degree of re-adsorption and hydrogenation of α-olefins [22]. The increased formation of CO_2 is likely due to the increased H_2O partial pressure at higher conversions, leading to a higher potential of re-oxidation of cobalt metal, which resulted in an increased rate of the WGS reaction. The Co WGS activity will be discussed in the separate chapter.

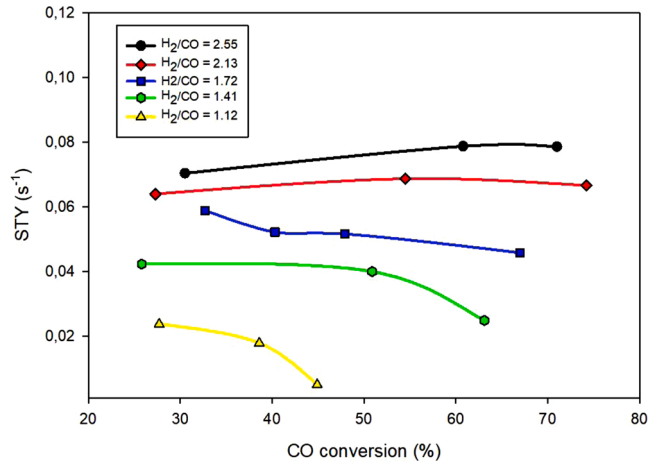

Fig. 2. Catalyst activity reported as site time yields (STY) vs CO conversion with different H_2/CO ratios at 210 °C and 20 bar.

3.2.2. Effect of feed gas composition

The effect of feed gas composition on the kinetics of the Fischer-Tropsch synthesis is well established, where the rate of reaction increases with increasing H_2/CO ratio [23]. The molar H_2/CO usage ratio is 2.06:1 for heavier hydrocarbons (waxes) [24]. Hence, using synthesis gas ratios lower than that will create a hydrogen deficiency for the reactions at increasing conversion, lowering the theoretical limit of CO conversion [25]. The Co activity, described as the STY, versus CO conversion is presented in Fig. 2. The STY is almost constant with the changes in conversion for the H_2/CO ratios higher than 1.7. For the lower H_2/CO ratios, the STY has a decreasing trend. The gradient in the partial pressures of H_2 and CO over the catalyst bed could contribute to this behavior. With H_2/CO ratio of 1 and a CO conversion level of 47 %, hydrogen will be nearly depleted at the end of the catalyst bed. This decreasing trend in STY is in agreement with the previously published work form our group [25].

A comparison of the selectivities at the various feed gas compositions and two temperatures at approximately 50 % CO conversion is presented in Table 1. Increasing the H_2/CO ratio leads to increased methane formation and decreased CO_2, C_{5+} and a reduced olefin-to-paraffin ratio for the intermediate hydrocarbons (C_2 - C_4). Lillebø et al. [25] reported a nearly linear relationship between the C_{5+} selectivity and the syngas composition. The highest C_{5+} was found for the lowest H_2/CO ratio, 87 % and 85.8 % for 210 °C and 230 °C, respectively. Varying the H_2/CO ratio shifts the surface concentrations of adsorbed species, i.e. a lower H_2/CO ratio gives a lower surface concentration of hydrogen and higher concentration of -CH_2 monomer [26]. This materializes as a higher chain-growth probability and lower hydrogenation activity, consequently favoring the formation of olefins and heavier hydrocarbons prior to methane and saturated hydrocarbon chains. The highest CO_2 selectivity of 12 % was obtained for the lowest H_2/CO ratio of 1.12, indicating a significant WGS activity.

Table 1
FT product selectivities at approximately 50 % CO conversion[c] with different H_2/CO ratios and different temperatures.

H_2/CO	Flow rate (ml/min)		S_{CO2} (%)		S_{CH4} (%)		S_{C5+}[a] (%)		O/P[b]	
	210 °C	230 °C	210 °C	230 °C	210 °C	230 °C	210 °C	230 °C	210 °C	230 °C
1.12	32.7	37.5	12	12.9	3.9	5.5	87.0	85.8	2.8	2.1
1.41	120	90	0.6	1.1	6.0	7.7	86.6	85.3	2.1	1.5
1.73	150	190	0.3	0.5	8.0	10.1	84.0	81.2	1.4	1.0
2.13	134	100	0.2	0.4	9.4	11.8	81.0	79.2	1.3	0.8
2.55	140	135	0.2	0.4	10.9	14.1	79.4	76.2	1.1	0.7

[a] Reported on a CO_2 free basis.
[b] Total olefin-to-paraffin ratio for C_2-C_4 species.
[c] CO conversion = 49 +/- 3%.

Table 2
Effect of adding water (2 bar water added) on STY at different feed gas compositions at constant flow of 250 mL/min.

H_2/CO	STY (s^{-1})			
	210 °C		230 °C	
	Dry feed	With water	Dry feed	With water
2.55	0,060	0,066	0,14	0,17
2.13	0,050	0,054	0,13	0,15
1.72	0,046	0,048	0,13	0,15
1.41	0,030	0,030	0,073	0,088
1.12	0,019	0,016	0,054	0,047

3.2.3. *Effect of temperature*

Fischer-Tropsch product selectivities are dependent on temperature, Table 1. Experiments performed at 230 °C obtained higher methane selectivity for all H_2/CO ratios with the highest (14.1 %) obtained with the H_2/CO ratio of 2.55 at 230 °C. Hence, the combined effects of temperature and the feed gas ratio has a strong influence on the methane selectivity. The rate of the hydrogenation reaction of -CH_2 monomers (to methane) is increasing faster with temperature than its competing reactions, thus lowering the surface concentration of -CH_2 monomers [27]. This is supported by the observed decreased olefin-to-paraffin ratios with increased temperature, indicating also a higher relative rate of olefin hydrogenation. Pendyala et al. [28] performed experiments on aqueous-phase Fischer-Tropsch synthesis and observed a higher rate of formation of both methane and CO_2 and a lower rate of formation of heavier hydrocarbons when increasing the temperature. Higher temperatures also increase the WGS reaction.

3.2.4. *Effect of added water*

The addition of external water is a common strategy for simulating high conversion levels without altering the residence time, as the partial pressure of water is increased. An additional 2 bar of water was added while keeping the syngas flow at 250 mL/min We observed all positive, negative and neutral effects of water on the activity, with no obvious trend what dictates the effect, Table 2. In most cases, the addition of water yields an immediate positive response in activity followed by a steady decline (see Figs. 1 and S2–S4 in the supplementary information). The negative effect was found for the lowest H_2/CO ratio of 1.41, Fig. S1. The effect of water seems to be almost independent on temperature.

Blekkan *et al.* [29] reported positive, negative and neutral effects of water on activity which indicates that the results can be conflicting. Borg et al. [30] performed experiments on a set of catalysts with different pore characteristics, where positive effects were observed only for wide-pore catalysts, while negative effects were reported over narrow-pore catalysts. Their concluding remark was that the kinetic effect of external water was likely determined by the pore characteristics. Rytter et al. [31] reported that catalysts with broad pore size distributions were more susceptible to displaying negative effects of external water on the kinetics, while the opposite was true for catalysts with wider pores, and sufficiently large cobalt crystallites. The size of the cobalt particles is another factor highly influencing the selectivities, where it is reported that the catalyst with the smaller cobalt particle size had a lower catalytic activity and C_{5+} selectivity [32]. Borg et al. [13] found that the C_{5+} selectivity increased with increasing particle size.

Since all experiments were performed on the same catalyst, it is expected that the pore structure variation is negligible between the batches. Hence, the various feed gas compositions must either influence the pore structure differently during the reaction, or the kinetic effect of water must be more complex than solely a pore characteristics phenomenon.

The water effect on selectivities is, however, more straightforward. Except for the experiment with H_2/CO = 1.12 at 210 °C, the C_{5+}, CO_2, and olefin-to-paraffin selectivity is increased when feeding water, while methane formation was decreased. Storsæter et al. [14] found both increased C_{5+} selectivity and decreased selectivity to methane on both promoted and unpromoted cobalt catalysts supported on titania, silica, and alumina. This can be explained if some of the methane is formed on special methanation sites where chain growth cannot take place [33], where water may inhibit the reaction kinetics over these methanation sites, but not the traditional FT sites where the bulk of the hydrocarbons are formed. Another explanation could be that water does affect the polymerization kinetics if, for example, it promotes carbon-carbon coupling or retards chain termination via hydrogenation [34]. There might be a possibility that some fraction of the indigenous water could be in the liquid phase in the pores of the Co-based catalyst due to capillary condensation under relevant FT condition. Thus, water in a liquid phase may change the transportation of the reactants (H_2 and CO) from the bulk phase to the catalyst active sites, and consequently, change the reaction rate and product selectivity [35].

There are hardly any differences in the selectivity towards CH_4, C_{5+},

Table 3
Effect of indigenous and added water on FTS, H_2/CO = 2.13, T = 210 °C.

Effect of water	TOS (h)	STY (10^2 s^{-1})	Flow rate (ml/min)	Conversion (%)	S_{CO2} (%)	S_{CH4} (%)	S_{C5+}[a] (%)	O/P[b] (%/%)
indigenous	56.7	6.3	95.6	70.5	0.27	8.3	82.6	1.05
added	132.3	4.9	113.96[c]	70.8	0.45	7.4	83.7	1.77

[a] Reported as CO_2 free.
[b] Total olefin-to-paraffin ratio for C_2-C_4 species.
[c] Included 10.36 mL/min water.

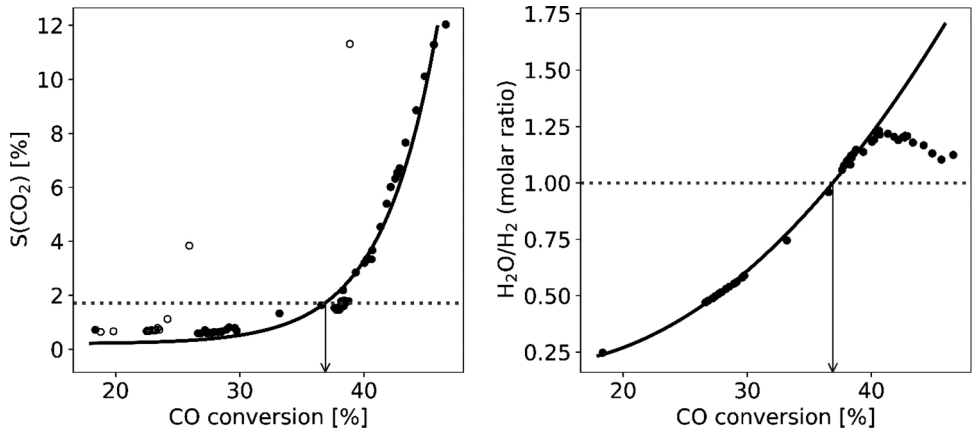

Fig. 3. Relationships between the CO_2 selectivity and CO conversion (left panel), and molar ratio of H_2O and H_2 (right panel) when adding water to the feed. Filled symbols represent data points collected when increasing the conversion, while open symbols denote the return to low conversions. Conditions: $H_2/CO = 1.12$, $m_{cat.} = 4.0$ g, T = 210 °C, p =20 bar.

and CO_2 when comparing indigenous and added water at quite similar and comparable syngas flows, Table 3. There is, however, a clear difference in selectivity towards olefins versus paraffins. As was discussed previously, the probability of secondary reactions taking place, including re-adsorption and hydrogenation of olefins to form paraffins, are highly dependent on the residence time. However, when simulating high conversion by adding external water to the feed, the residence time is as good as unchanged, and in this case, the olefin to-paraffin ratio increased. When lowering the feed flow rate whilst feeding water, it is observed that the olefin-to-paraffin ratio decreases. This suggests that the effects of residence time and water addition are two conflicting phenomena, where water has an inhibiting effect on secondary hydrogenation of olefins, while the opposite is true for residence time. This is a result of the combined contributions of a lower rate of chain termination via hydrogen addition and a lower rate of secondary hydrogenation reactions [22]. It is, however, important to emphasize that the two scenarios are not directly comparable, as the concentration profile of water throughout the reactor is more uniform in the case where external water is fed, whilst in the case where no water is added, the concentration of indigenous water will be high only near the exit of the reactor.

3.2.5. *Water-gas shift activity for the Co based catalyst*

Cobalt-based catalysts are often claimed to display negligible or low activity towards the WGS reaction [36]. However, Marion et al. [12] performed experiments at high conversions to induce WGS activity. They reported that cobalt catalysts WGS activity is dependent on the specific criterion molar ratio H_2O/H_2 in the reactor. Thus, Co catalyst would develop significant WGS activity if the ratio exceeds 1. They also observed that the process was both reversible and that the reversibility was close to instantaneous, and hence favored a hypothesis for the modification in selectivity (WGS versus FTS) based on the competition between H_2 and H_2O to react with CO.

This phenomenon was observed in the experiments performed with a H_2/CO ratio of 1.12 for both temperatures (210 °C, 230 °C). The effect was diminishing as the H_2/CO ratio was increased. The experiment at 210 °C and $H_2/CO = 1.12$ is used as an illustration here, Fig. 3. The highest selectivity to CO_2 reached maximum of about 12 % at 46.6 % conversion. The right-hand plot in Fig. 3 shows the calculated molar ratio of H_2O and H_2 at the reactor outlet plotted as a function of CO conversion. The H_2O/H_2 molar ratio exceeds unity at the higher conversions. Comparing the molar ratio with the plot of the selectivity to CO_2 as a function of CO conversion, as shown in the left-hand graph, it is evident that when the H_2O/H_2 ratio exceeds unity the CO_2 selectivity increases dramatically, indicating increasing WGS activity. The figure also shows the reversibility of the phenomenon, where a rapid decline in CO_2 selectivity (and hence WGS activity) is observed and the selectivity to CO_2 is fully reversed shortly after lowering the conversion level. There is however a hysteresis effect, the CO_2 selectivity curve is upon reducing the CO conversion clearly higher than the one resulting from increasing the conversion. This could indicate that a change in the catalyst properties is involved such as formation of cobalt oxides. However, another pathway for CO_2 formation may also be of relevance here. The

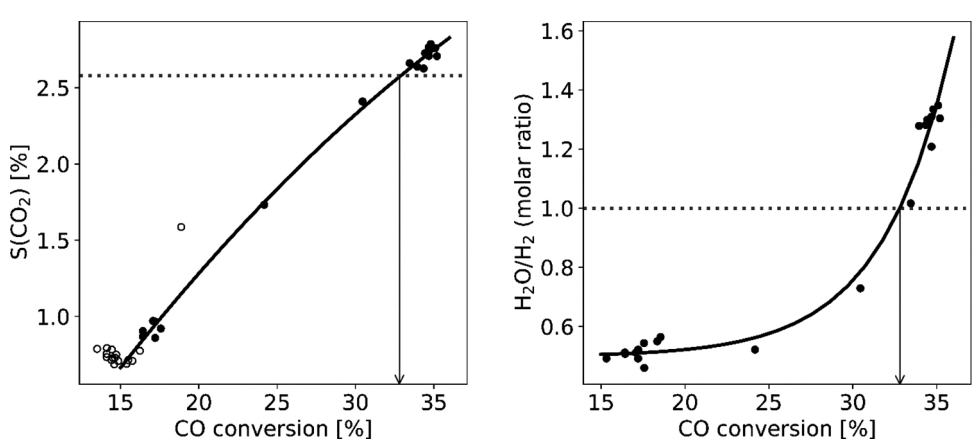

Fig. 4. Relationships between the CO_2 selectivity and CO conversion (left panel), and molar ratio of H_2O and H_2 (right panel) when adding water to the feed. Filled symbols represent data points collected when increasing the conversion, while open symbols denote the return to low conversions. Conditions: $H_2/CO = 1.12$, $m_{cat.} = 4.0$ g, T = 210 °C. The pressure was 22 bar (20 bar syngas and 2 bar water) in instances with filled symbols, and 20 bar for the hollow symbols.

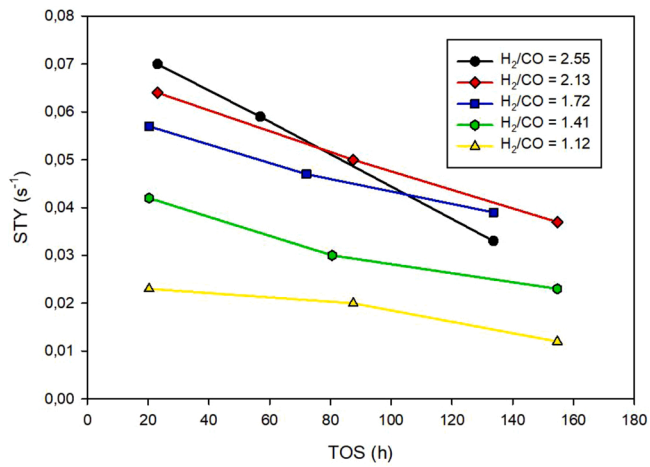

Fig. 5. Catalyst deactivation with different feed gas composition at constant flow of 250 mL/min at 210 °C and 20 bar.

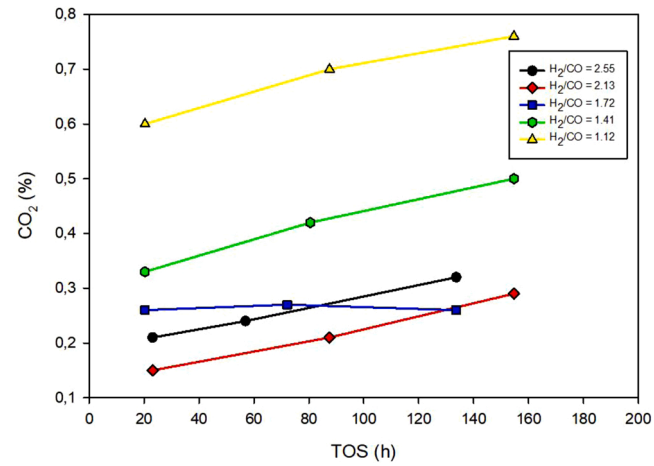

Fig. 6. CO_2 selectivity with TOS at constant flow (250 mL/min) with different H_2/CO ratios at 210 °C and 20 bar.

Boudouard reaction is a disproportionation reaction of carbon monoxide into CO_2 and elemental carbon, and although it is favored at higher temperatures than those under investigation here [11], it is possible that this pathway may be relevant under these extreme hydrogen depleted conditions. Considering that the elemental carbon formed in the Boudouard reaction would deposit onto the surface of the catalyst and cause fouling, a notable drop in kinetic activity would be observed if this reaction was significant. This was, however, not observed given that the topical experiment displayed the lowest degree of deactivation of all experiments. Hence, it is not likely that the Boudouard reaction plays a significant role in the formation of CO_2 in this instance, such that cobalt re-oxidation arises as the preferred hypothesis to explain the phenomenon.

The effect is, however, not as substantial when water was added to the feed, as indicated in Fig. 4. In this case, it was not possible to reach the same conversion level as was reached at "dry" conditions and still maintaining the pressure in the reactor, hence the maximum obtained conversion was about 35 %. Still, with the added water the higher conversion is simulated. Considering this, it would be expected that the response in activity for the WGS reaction would approximate that observed during the "dry" conditions, but the trends are quite different. Although adding water to the feed is not exactly analogous to that of increased conversion level given both the different water pressure gradient throughout the reactor and the differences in the amounts of H_2 and CO present, this result is rather surprising. Concerning the hypothesis that re-oxidized cobalt is the main cause of the formation of CO_2 through WGS activity, this result implies that either does the externally added water act differently than indigenous water or that the higher concentration of CO and H_2 present while adding water reduces the potential for re-oxidizing. This is supported when cobalt activity is compared for two situations. At 'dry' conditions at 46.6 % conversion, the STY was just 0.004 (s^{-1}), indicating strong deactivation induced by indigenous water. On the other hand, when water is added (35 % conversion) the STY was 0.01 (s^{-1}), indicating a weaker response to the added water.

3.2.6. Catalyst deactivation

The deactivation rate is dependent on the reaction conditions. Several deactivation mechanisms have been proposed, whereas two main mechanisms are somewhat observable during FTS experiments, namely re-oxidation of metallic cobalt and sintering [9]. We observed decreased STY over time on stream for all H_2/CO ratios at constant syngas flow of 250 mL/min for both temperatures investigated. Comparison of the slopes of the deactivation curves at the various feed gas ratios shows a trend where the catalyst suffers less deactivation as the

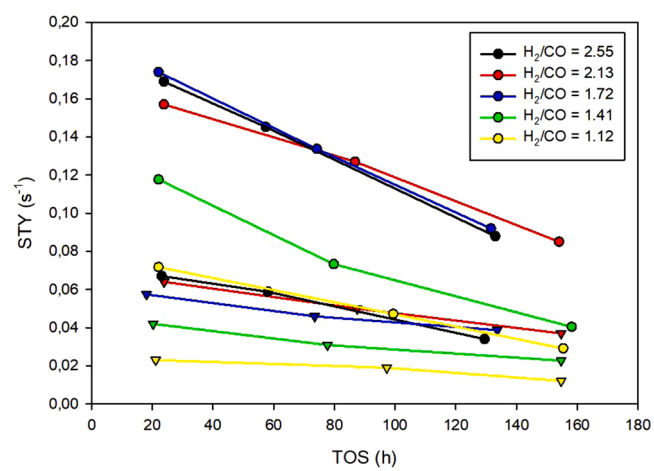

Fig. 7. Catalyst activity reported as STY vs time on stream for different H_2/CO ratios at 250 mL/min at 210 °C (triangles) and 230 °C (circles).

H_2/CO ratio is decreased, Fig. 5. The deactivation curves include periods with high conversion and added water feed to the syngas, but the points showing the activity were collected at the constant 'dry' syngas feed rate, at various times during the experiment.

Water, as the most abundant product in Fischer-Tropsch synthesis, is an oxidizing agent, and although bulk oxidation of metallic cobalt is thermodynamically infeasible under realistic FTS conditions [37], it has been calculated that very small surface cobalt particles may behave differently [38]. Peterson et al. [39] reported that water hinders the reduction of cobalt oxide with shifting transition temperatures, where the transition of CoO to Co° was particularly slowed. Wolf et al. [40] reported formation of inactive cobalt aluminate induced by high water partial pressure (p_{H2O}/p_{H2} ratio of 30). Since in the present work that high levels were not reached, the formation of cobalt aluminate as a source for catalyst deactivation is less likely. Considering that sintering is mainly a function of temperature [41] and that coking is more critical at low H_2/CO ratios [9], it is probable that the re-oxidation of small cobalt particles is a cause of deactivation. Re-oxidation causes phase transformation of metallic cobalt to FT inactive cobalt oxides, resulting in fewer active cobalt sites on the catalyst, thus negatively affecting the activity. Schanke et al. [37] studied the role of water on deactivation on alumina supported cobalt Fischer-Tropsch catalysts using XPS studies and they observed significant surface oxidation of cobalt even at low H_2O/H_2 ratios and concluded that surface oxidation or oxidation of

Table 4
Summary of the observed effect of the various conditions.

Parameter	Chain growth	Olefin selectivity	CO_2 selectivity	CH_4 selectivity	Rate of deactivation	STY
Temperature	↓	↓	↑	↑	↑	↑
H_2/CO ratio	↓	↓	↓	↑	↑	↑
Water addition	↑	↑	↑	↓	↑	*
CO conversion	↑	↓	↑	↓	*	*

(↑) Increasing with increasing parameter.
(↓) Decreasing with increasing parameter.
(*) Inconclusive/minimal effect.

highly dispersed cobalt phases was responsible for the observed deactivation. This is supported by the increased CO_2 selectivity for all H_2/CO ratios (except 1.72) due to the pronounced WGS activity with time on stream, Fig. 6.

We have also observed a steeper deactivation curve for all H_2/CO ratios when increasing temperature to 230 °C, Fig. 7. The filled circles represent the points at 230 °C, while the triangles represent points at 210 °C. We can observe that higher H_2/CO ratios result in steeper deactivation curves. FTS is a highly exothermic reaction and therefore operating the lab-reactor at isothermal conditions is important. Fixed-bed reactors can have poor heat transfer rates and hot spots may arise during operation, thus, the potential for sintering is relatively high [9]. Sintering of cobalt particles leads to an overall reduction of the active surface area, resulting in lower reaction rates. Both sintering and re-oxidation of cobalt particles are highly dependent on the temperature [9]. Claeys et al. [42] studied the impact of process conditions on sintering in Fischer-Tropsch synthesis on a platinum promoted alumina supported cobalt catalyst and used *in-situ* magnetic measurements. The authors concluded that sintering occurred via a combination of high CO and high water partial pressures. Hence, it appears that sintering is the prominent deactivation mechanism in the early stages of operation. This phenomenon has also been reported by Sadeqzadeh et al. [43], suggesting that sintering was the main reason for initial deactivation, while a combination of surface oxidation and carbon deposition mainly caused long-term deactivation.

4. Conclusion

The commercial type 20 %Co/0.5Re γ-Al_2O_3 Fischer-Tropsch catalyst was tested at a variety of process conditions, including a range of feed gas compositions, variation in the conversion level, water addition, and different temperatures. Based on the observations made during all the experiments in this work, a summary of all the reaction conditions and how they influence the FTS are given in Table 4.

CRediT authorship contribution statement

Ljubiša Gavrilović: Investigation, Validation, Supervision, Writing - original draft. **Erik A. Jørgensen:** Investigation, Visualization. **Umesh Pandey:** Methodology, Writing - review & editing. **Koteswara R. Putta:** Methodology, Writing - review & editing. **Kumar R. Rout:** Conceptualization, Methodology, Validation. **Erling Rytter:** Conceptualization, Methodology, Validation. **Magne Hillestad:** Writing - review & editing, Conceptualization, Methodology, Validation. **Edd A. Blekkan:** Conceptualization, Methodology, Supervision, Validation, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.07.055.

References

[1] M.E. Dry, The Fischer-Tropsch process: 1950-2000, Catal. Today (2002) 227–241, https://doi.org/10.1016/S0920-5861(01)00453-9.
[2] R. Rauch, A. Kiennemann, A. Sauciuc, Fischer-Tropsch synthesis to biofuels (BtL process). Role Catal. Sustain. Prod. Bio-Fuels Bio-Chemicals, Elsevier Inc., 2013, pp. 397–443.
[3] E. van Steen, M. Claeys, Fischer-Tropsch catalysts for the biomass-to-liquid process, Chem. Eng. Technol. 31 (2008) 655–666.
[4] A.H. Lillebø, A. Holmen, B.C. Enger, E.A. Blekkan, Fischer-Tropsch conversion of biomass-derived synthesis gas to liquid fuels. Adv. Bioenergy Sustain. Chall., Wiley Blackwell, 2015, pp. 131–147.
[5] R.C. Baliban, J.A. Elia, C.A. Floudas, Biomass to liquid transportation fuels (BTL) systems: process synthesis and global optimization framework, Energy Environ. Sci. 6 (2013) 267–287, https://doi.org/10.1039/c2ee23369j.
[6] S.S. Ail, S. Dasappa, Biomass to liquid transportation fuel via Fischer Tropsch synthesis - Technology review and current scenario, Renew. Sustain. Energy Rev. 58 (2016) 267–286.
[7] A.N. Stranges, A history of the fischer-tropsch synthesis in Germany 1926-45. Stud. Surf. Sci. Catal., 2007, pp. 1–27, https://doi.org/10.1016/S0167-2991(07)80469-1.
[8] A.Y. Khodakov, W. Chu, P. Fongarland, Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels, Chem. Rev. 107 (2007) 1692–1744, https://doi.org/10.1021/cr050972v.
[9] N.E. Tsakoumis, M. Rønning, Ø. Borg, E. Rytter, A. Holmen, Deactivation of cobalt based Fischer-Tropsch catalysts: a review, Catal. Today (2010) 162–182.
[10] C.M. Balonek, A.H. Lillebø, S. Rane, E. Rytter, L.D. Schmidt, A. Holmen, Effect of alkali metal impurities on Co-Re catalysts for Fischer-Tropsch synthesis from biomass-derived syngas, Catal. Lett. 138 (2010) 8–13.
[11] M.E. Dry, Chapter 7 – FT catalysts. Stud. Surf. Sci. Catal, Elsevier, 2004, pp. 533–600, https://doi.org/10.1016/S0167-2991(04)80464-6.
[12] M.C. Marion, F. Hugues, Modification of cobalt catalyst selectivity according to fischer-tropsch process conditions, Stud. Surf. Sci. Catal. 167 (2007) 91–96, https://doi.org/10.1016/S0167-2991(07)80114-5.
[13] Ø. Borg, N. Hammer, S. Eri, O.A. Lindvåg, R. Myrstad, E.A. Blekkan, M. Rønning, E. Rytter, A. Holmen, Fischer-Tropsch synthesis over un-promoted and Re-promoted γ-Al2O3 supported cobalt catalysts with different pore sizes, Catal. Today 142 (2009) 70–77.
[14] S. Storsæter, Borg, E.A. Blekkan, A. Holmen, Study of the effect of water on Fischer-Tropsch synthesis over supported cobalt catalysts, J. Catal. 231 (2005) 405–419, https://doi.org/10.1016/j.jcat.2005.01.036.
[15] J. Li, G. Jacobs, Y. Zhang, T. Das, B.H. Davis, Fischer-Tropsch synthesis: effect of small amounts of boron, ruthenium and rhenium on Co/TiO2 catalysts, Appl. Catal. A Gen. 223 (2002) 195–203, https://doi.org/10.1016/S0926-860X(01)00752-9.
[16] A. Ali, M. Ali, Effects of different loadings of Ru and Re on physico- chemical properties and performance of 15% Co/Al 2 O 3 FTS catalysts, Iran. J. Chem. Chem. Eng. 24 (2005) (Accessed 6 September 2017), http://www.ijcce.ac.ir/article_8111_a2bb25a626dcbdace44e4d5e21718dbb.pdf.
[17] C.E. Kliewer, S.L. Soled, G. Kiss, Morphological transformations during Fischer-Tropsch synthesis on a titania-supported cobalt catalyst, Catal. Today 323 (2018) 233–256, https://doi.org/10.1016/j.cattod.2018.05.021.
[18] L. Gavrilović, J. Brandin, A. Holmen, H.J. Venvik, R. Myrstad, E.A. Blekkan, Fischer-Tropsch Synthesis – investigation of the deactivation of a Co catalyst by exposure to aerosol particles of potassium salt, Appl. Catal. B Environ. 230 (2018) 203–209, https://doi.org/10.1016/j.apcatb.2018.02.048.
[19] L. Gavrilović, J. Brandin, A. Holmen, H.J. Venvik, R. Myrstad, E.A. Blekkan, Deactivation of co-based Fischer–Tropsch catalyst by aerosol deposition of

potassium salts, Ind. Eng. Chem. Res. 57 (2018) 1935–1942, https://doi.org/10.1021/acs.iecr.7b04498.
[20] A.M. Hilmen, D. Schanke, A. Holmen, TPR study of the mechanism of rhenium promotion of alumina-supported cobalt Fischer-Tropsch catalysts, Catal. Lett. 38 (1996) 143–147, https://doi.org/10.1007/BF00806560.
[21] W. Ma, G. Jacobs, Y. Ji, T. Bhatelia, D.B. Bukur, S. Khalid, B.H. Davis, Fischer-Tropsch synthesis: influence of CO conversion on selectivities, H2/CO usage ratios, and catalyst stability for a ru promoted Co/Al2O3 catalyst using a slurry phase reactor, Top. Catal. 54 (2011) 757–767, https://doi.org/10.1007/s11244-011-9699-5.
[22] S. Krishnamoorthy, M. Tu, M.P. Ojeda, D. Pinna, E. Iglesia, An investigation of the effects of water on rate and selectivity for the Fischer-Tropsch synthesis on cobalt-based catalysts, J. Catal. 211 (2002) 422–433, https://doi.org/10.1006/jcat.2002.3749.
[23] G.P. Van Der Laan, A.A.C.M. Beenackers, Kinetics and selectivity of the Fischer–Tropsch synthesis: a literature review, Catal. Rev. 41 (1999) 255–318, https://doi.org/10.1081/CR-100101170.
[24] D. Tristantini, S. Løgdberg, B. Gevert, Øyvind Borg, A. Holmen, The effect of synthesis gas composition on the Fischer-Tropsch synthesis over Co/ɣ-Al2O3 and Co-Re/ɣ-Al2O3 catalysts, Fuel Process. Technol. 88 (2007) 643–649.
[25] A. Lillebø, E. Rytter, E.A. Blekkan, A. Holmen, Fischer-Tropsch synthesis at high conversions on Al2O3-supported co catalysts with different H2/CO levels, Ind. Eng. Chem. Res. 56 (2017) 13281–13286, https://doi.org/10.1021/acs.iecr.7b01801.
[26] E. Rytter, N.E. Tsakoumis, A. Holmen, On the selectivity to higher hydrocarbons in Co-based Fischer-Tropsch synthesis, Catal. Today 261 (2016) 3–16.
[27] M.E. Dry, Practical and theoretical aspects of the catalytic Fischer-Tropsch process, Appl. Catal. A Gen. 138 (1996) 319–344, https://doi.org/10.1016/0926-860X(95)00306-1.
[28] V.R.R. Pendyala, W.D. Shafer, G. Jacobs, B.H. Davis, Fischer-Tropsch synthesis: effect of reaction temperature for aqueous-phase synthesis over a platinum promoted co/alumina catalyst, Catal. Lett. 144 (2014) 1088–1095, https://doi.org/10.1007/s10562-014-1247-z.
[29] E.A. Blekkan, Ø. Borg, V. Frøseth, A. Holmen, Fischer-Tropsch Synthesis on Cobalt Catalysts: The Effect of Water, Royal Society of Chemistry, Cambridge, 2007, https://doi.org/10.1039/9781847558442.
[30] Ø. Borg, S. Storsæter, S. Eri, H. Wigum, E. Rytter, A. Holmen, The effect of water on the activity and selectivity for γ-alumina supported cobalt Fischer-Tropsch catalysts with different pore sizes, Catal. Lett. 107 (2006) 95–102, https://doi.org/10.1007/s10562-005-9736-8.
[31] E. Rytter, Ø. Borg, N.E. Tsakoumis, A. Holmen, Water as key to activity and selectivity in Co Fischer-Tropsch synthesis: Γ-alumina based structure-performance relationships, J. Catal. 365 (2018) 334–343, https://doi.org/10.1016/j.jcat.2018.07.003.
[32] L. Gavrilović, J. Save, E.A. Blekkan, The effect of potassium on cobalt-based Fischer-Tropsch catalysts with different cobalt particle sizes, Catalysts 9 (2019) 351, https://doi.org/10.3390/catal9040351.
[33] H. Schulz, M. Claeys, S. Harms, Effect of water partial pressure on steady state Fischer-Tropsch activity and selectivity of a promoted cobalt catalyst, Stud. Surf. Sci. Catal. 107 (1997) 193–200, https://doi.org/10.1016/S0167-2991(97)80334-5.
[34] F.G. Botes, B. Van Dyk, C. McGregor, M. Claeys, E. van Steen, F.G. Botes, On the effect of water during Fischer-Tropsch synthesis with a ruthenium catalyst, Ind. Eng. Chem. Res. 48 (2009) 419–427, https://doi.org/10.1016/S0920-5861(01)00469-2.
[35] C.G. Okoye-Chine, M. Moyo, X. Liu, D. Hildebrandt, A critical review of the impact of water on cobalt-based catalysts in Fischer-Tropsch synthesis, Fuel Process. Technol. 192 (2019) 105–129, https://doi.org/10.1016/j.fuproc.2019.04.006.
[36] E. Rytter, A. Holmen, Deactivation and regeneration of commercial type Fischer-Tropsch co-catalysts—a mini-review, Catalysts 5 (2015) 478–499, https://doi.org/10.3390/catal5020478.
[37] D. Schanke, A.M. Hilmen, E. Bergene, K. Kinnari, E. Rytter, E. Ådnanes, A. Holmen, Reoxidation and deactivation of supported cobalt Fischer–Tropsch catalysts, Energy Fuels 10 (1996) 867–872, https://doi.org/10.1021/ef950197u.
[38] E. Van Steen, M. Claeys, M.E. Dry, J. Van De Loosdrecht, E.L. Viljoen, J.L. Visagie, Stability of nanocrystals: thermodynamic analysis of oxidation and re-reduction of cobalt in water/hydrogen mixtures, J. Phys. Chem. B 109 (2005) 3575–3577, https://doi.org/10.1021/jp045136o.
[39] J. Paterson, M. Peacock, E. Ferguson, M. Ojeda, J. Clarkson, In situ X-ray diffraction of Fischer-Tropsch catalysts—effect of water on the reduction of cobalt oxides, Appl. Catal. A Gen. 546 (2017) 103–110, https://doi.org/10.1016/j.apcata.2017.08.017.
[40] M. Wolf, E.K. Gibson, E.J. Olivier, J.H. Neethling, C.R.A. Catlow, N. Fischer, M. Claeys, Water-induced formation of cobalt-support compounds under simulated high conversion Fischer-Tropsch environment, ACS Catal. 9 (2019) 4902–4918, https://doi.org/10.1021/acscatal.9b00160.
[41] G. Ertl, H. Knözinger, J. Weitkamp, Handbook of Heterogeneous Catalysis, 2008 (Accessed 13 September 2019), https://pdfs.semanticscholar.org/e395/088acee9fc3a3f1893c3116a1a66b7bb96da.pdf.
[42] M. Claeys, M.E. Dry, E. Van Steen, P.J. Van Berge, S. Booyens, R. Crous, P. Van Helden, J. Labuschagne, D.J. Moodley, A.M. Saib, Impact of process conditions on the sintering behavior of an alumina-supported cobalt Fischer-Tropsch catalyst studied with an in situ magnetometer, ACS Catal. 5 (2015) 841–852, https://doi.org/10.1021/cs501810y.
[43] M. Sadeqzadeh, S. Chambrey, J. Hong, P. Fongarland, F. Luck, D. Curulla-Ferré, D. Schweich, J. Bousquet, A.Y. Khodakov, Effect of different reaction conditions on the deactivation of alumina-supported cobalt Fischer-Tropsch catalysts in a milli-fixed-bed reactor: experiments and modeling, Ind. Eng. Chem. Res. 53 (2014) 6913–6922, https://doi.org/10.1021/ie4040303.