

H₂-poor bio-syngas in Fischer-Tropsch synthesis over un-promoted and rhenium promoted alumina-supported cobalt catalysts: Effect of water addition

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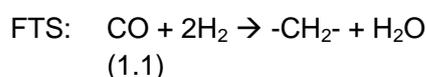
The effect of water addition on Fischer-Tropsch synthesis (FTS) over 12%Co/Al₂O₃ and 12%Co-0.5%Re/Al₂O₃ catalysts was investigated in a fixed bed reactor with model mixtures of biomass-derived syngas (bio-syngas). The bio-syngas model mixtures consist of H₂ and CO of different molar H₂/CO-ratios (1.0, 1.5 and 2.1). The FT-reaction requires a H₂/CO molar ratio of approximately 2.1 above the catalyst surface. For the ratios lower than 2.1, an *in situ* water-gas shift (WGS) activity is desired in order to increase the H₂/CO-ratio. However, the studied catalysts had quite low WGS activities. The addition of water slightly increased the WGS activity for all types of bio-syngases and for both catalysts. The highest WGS activity was found for the un-promoted Co-catalyst at the inlet H₂/CO-ratio = 1.0. Water addition also results in an increase in selectivity to C₅₊ and a decrease in selectivity to CH₄. Interestingly, for both of catalysts the selectivity to C₅₊ and CH₄ were rather similar for inlet H₂/CO-ratios of 2.1 and 1.5, while the highest selectivity to C₅₊ and the lowest selectivity to CH₄ were also found for the inlet ratio = 1.0. All catalysts were deactivated by water addition but the catalyst activity is partly recovered in H₂/CO-ratio inlets = 1.0 and 1.5. The Co/Al₂O₃ was affected by water more severely in H₂/CO-ratios = 2.1. The Re-promoted Co catalyst was considerably more active and selective to longer hydrocarbons than the un-promoted one.

The conclusion of this study is that in order to utilize the advantages of a bio-syngas with a low H₂ content (higher selectivity to C₅₊, lower selectivity to CH₄, no WGS-unit needed prior to FT-reactor), the catalyst must possess a much higher WGS activity than the ones studied.

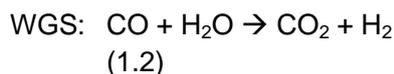
Keywords: Adsorption H₂-poor bio-syngas; Fischer-Tropsch Synthesis, Water-Gas Shift, Cobalt, Rhenium-Cobalt alumina, molar H₂/CO-ratios.

INTRODUCTION

The Fischer-Tropsch (FT) synthesis over cobalt-based catalyst produces mostly alkanes and 1-alkenes. The reaction stoichiometry approximated as :



Water is produced along with the desired products in FT reaction, however it is well known that cobalt is not very active for the water gas shift reaction (WGS).



Yates and Satterfield (1991) reported that only a small fraction of water produced in FT reaction was converting to CO_2 when cobalt is used in FTS, thus, in contrast to most iron-based catalysts. The WGS can increase or decrease the FTS rate because these reactions share the same component reactants, adsorption and desorption reactions as well as dissociation of H_2 , H_2O , and CO_2 , and reactions of formate species (Rofer-de-Poorter 1984). By the addition of water a high conversion can be simulated without using long residence time. Furthermore, the combination of low conversion and steam addition also results in a flat axial water concentration profile in the reactor, thus simulating the uniform bulk concentrations expected in large scale slurry reactors [Hilmen *et.al.* 1999]. More over, the cobalt catalysts are believed to deactivate less rapidly and yield a higher fraction of linear alkanes than their iron counterpart [Jacobs *et.al.* 2002].

Hilmen and co-workers (1999, 2001) observed Re-cobalt promoted catalyst deactivated severely by water than the un-promoted one. Studies in using cobalt on SiO_2 support catalysts gave different results while water added in FT reaction. Krishnamoorthy *et. al.* (2002) and Li *et. al.* (2002a) reported that water increased the activity whereas Minderhoud (1984) reported the opposite. According to Bertole (2002), water addition up to 40% to a functioning unsupported cobalt FT catalyst increased reactivity of adsorbed CO on the surface without changing the reactivity of the active surface carbon intermediate. This in turn leads to increase surface concentration of the monomeric carbon precursors to hydrocarbon formation. Recent study by Storsæter *et. al.* (2005a) using the H_2/CO -ratio = 2.1 reported that the catalyst activity after water was removed for both $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co-Re}/\text{Al}_2\text{O}_3$ returned to about the level observed when the 20 %

water added. It means some of the deactivation caused by water addition is reversible. The deactivation of these catalysts in the present of water is probably mostly due to re-oxidation of metallic cobalt [Zhang *et.al.* 1999, Schanke *et.al.* 1995].

In our previous study [Tristantini *et.al.*2006] we reported of using dry model mixtures for biomass-derived syngas (bio-syngas) with H_2/CO -ratio of 1.0, 1.5 and 2.1 on $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co-Re}/\text{Al}_2\text{O}_3$ catalysts. Adding water favors WGS reaction since water is a reactant for WGS. With that study we proved that there was only a small WGS activity in the FT-reaction when using dry feed. In continuation of our work we now report on the effect of water addition on the performance of those catalysts to produce hydrocarbons using similar model bio-syngases in order to achieve a beneficial of using syngas from biomass contains less H_2 in the mixture. The WGS activity is measured from the usage ratio and the selectivity to CO_2 while the activity of catalyst to FTS measured from conversion to hydrocarbon, selectivity to C_{5+} and selectivity to CH_4 . The conversion to hydrocarbons which based on the product of the reaction is a more suitable conversion to compare the activity of catalysts for different H_2/CO -ratio of syngases. The formulas we used to estimate the WGS activity and the conversion to hydrocarbon are similar that those in a previous report based on the FTS (1.1) and WGS (1.2) reactions [Tristantini *et.al.* 2006].

EXPERIMENTAL METHODS

Catalyst preparation

Catalysts 12% Co / Al_2O_3 and 12% Co / 0.5%Re / Al_2O_3 were prepared by incipient wetness co-impregnation method. Aqueous solutions containing 12 % cobalt and 0 % or 0.5 % rhenium of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HReO_4 was employed to alumina ($\gamma\text{-Al}_2\text{O}_3$) support. The γ -alumina support used was Puralox SCCa-5/200 from Sasol.

The classical drying process, calcinations and size reduction were described previously [Tristantini *et.al.*2006]. Reduction of catalyst was done *in situ*.

Catalytic reaction

Calcined catalysts (approximately 1 g) mixed with 4 g inert solid SiC (75-150 μm) were tested in a system comprising a stainless steel fixed bed reactor as described in the prior report [Tristantini *et.al.*2006]. The catalyst reduction was done *in situ* with a flowing of H_2 (200 $\text{cm}^3/\text{g}_{\text{cat}}\cdot\text{h}$) at atmospheric pressure and at temperature of 623 K for 16 hours with the heating rate 1 K/min from ambient temperature. The catalyst then was cooled to 443 K in H_2 flowing and flushed with He for another hour before the reactor system were pressurized to 20 bars and then the feed gas was introduced. The model bio-syngas feeds containing H_2 and CO of three different ratios of (H_2/CO) = 1.0, 1.5 and 2.1 were respectively premixed with 3 mol % N_2 as an internal standard. The reactor temperature was then slowly increased to the desired initial reaction temperature of 483 K. Product gases were analyzed on line by an HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) as describe in the prior report. The reaction was started (period 1) with initial space velocity was 200 cm^3/min (or GHSV=Gas Hold up Space Velocity= 12 $\text{Ndm}^3/\text{g}_{\text{cat}}\cdot\text{h}$) and then it was varied to achieve 25-30 % CO conversion for each type of bio-syngas (period 2). These two afore results had been reported previously [Tristantini *et.al.*2006]. Steam was added by evaporate distilled-water at 648 K which fed by a liquid flow controller. The water degassing beforehand by helium at least 16 h and the steam was mixed with synthesis gas just prior to the reactor inlet. The steam was added at pressure 5 bars (20%) and afterward 13 bars (33%) named period 3 and 4 respectively while the syngas was kept in the same space velocity. After

the water was stopped (period 5) the synthesis continued by using dry feed again with the same condition as in period 2 in order to see the catalyst deactivation after exposing water on the catalyst.

RESULT AND DISCUSSION

Effect of water addition and inlet H_2/CO -ratios on the FT- activities

As a reference here we show in Table 1 the result from the period 2 i.e. the dry feed (prior to any water addition) when the flow of inlet gas was fixed for remain of experiments. It is shown in table 1 that the syngas H_2/CO ratio = 1 had performance quite alike with the performance of syngas H_2/CO -ratio = 1.5; even the inlet H_2/CO -ratio = 1 has better conversion to hydrocarbon, hydrocarbon formation rate, selectivity to C_{5+} and C_3 (o/p) ratio and lower in selectivity to CH_4 . Continuing this work, we investigated how WGS activity and selectivity of hydrocarbon product change in different H_2/CO -ratio of syngases with the present of external water. The effect of water addition to hydrocarbon formation rate for different H_2/CO -ratio syngases as a function of time on stream for $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co-Re}/\text{Al}_2\text{O}_3$ are presented in Fig. 1 (A and B) respectively. It is seen from those figures that the water causes some deactivation, and the hydrocarbon formation rate is therefore followed as a function of time on stream. For the $\text{Co}/\text{Al}_2\text{O}_3$ in accordance with previous studies [Hilmen *et.al.* 1999 and 2001, Schanke *et.al.* 1995, Storsæter *et.al.* 2005a] using syngas H_2/CO -ratio =2.1, the hydrocarbon rate decreases with time on stream and the rate of deactivation increases when water is added (Fig. 1A). The reaction rates to hydrocarbons for syngases with H_2/CO -ratio = 1.5 and 1.0 were almost similar along the experiment time. They were also decreased by the addition of water but the decreases were not as much as that this for ratio inlet 2.1.

It was probably from the nature that the ratio syngases 1.5 and 1.0 were not so

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reactive compare to the ratio syngas 2.1. Before water addition, the reaction rates to hydrocarbons of 1.5 and 1.0 ratio inlets were only 33% of the reaction rate to hydrocarbons of 2.1 ratio inlet. After water was stopped the reaction rate to hydrocarbons for ratio 1.5 and 1.0 increase $\approx 20\%$ and for ratio 2.1 was almost unchanged. This means that catalyst deactivation caused by water addition is partly recovered for ratio inlets 1.5 and 1.0 but it is not for ratio 2.1. X-ray photo electron

spectra [Schanke *et.al.* 1995] have detected the oxidation of surface atoms in Co/Al₂O₃ catalyst exposed to high water concentration during FTS with ratio 2.1 syngas. Besides Al₂O₃, SiO₂ and TiO₂ were also used as supports [Storsæter *et.al.* 2005a] and for those two latter supported catalysts the decreases of hydrocarbon formation rate were not so much. In contrast some early workers [Kim 1993, Iglesia 1997, Schulz *et.al.* 1994] found water increased FTS rate on Co/ SiO₂.

Table 1.

Conversion to hydrocarbon, selectivity and activity of catalysts Co/Al₂O₃ and CoRe/Al₂O₃ prior to any water addition for different (H₂/CO)-ratio syngases at initial condition, $P_{Tot} = 20$ bars, $T = 483$ K

Syngas	(H ₂ /CO)=1.0		(H ₂ /CO)=1.5		(H ₂ /CO)=2.1	
	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃
GHSV [Ndm ³ /g.h]	3.0	4.4	3.0	6.0	6.3	8.8
Catalyst	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃	Co/Al ₂ O ₃	CoRe/Al ₂ O ₃
Conversion to HC [%]	38.86	41.61	39.24	37.62	31.82	31.34
Hydrocarbon formation rate [g _{HC} /g _{cat} .h]	0.21	0.34	0.21	0.42	0.37	0.50
TOF.10 ² (1/s)	2.97	3.28	2.99	4.03	5.09	4.85
Selectivity to CH ₄ [%]	5.98	5.92	8.93	8.02	10.72	9.15
Selectivity to C ₅₊ [%]	86.55	86.27	81.90	83.04	80.16	82.07
C ₃ (olefin/paraffin)	3.44	3.89	2.80	2.73	2.27	2.66
Selectivity to CO ₂ [%]	1.58	1.09	1.31	1.16	0.93	0.79
Usage ratio	2.02	2.03	2.06	2.06	2.09	2.08

^a Calculated from CO chemisorption

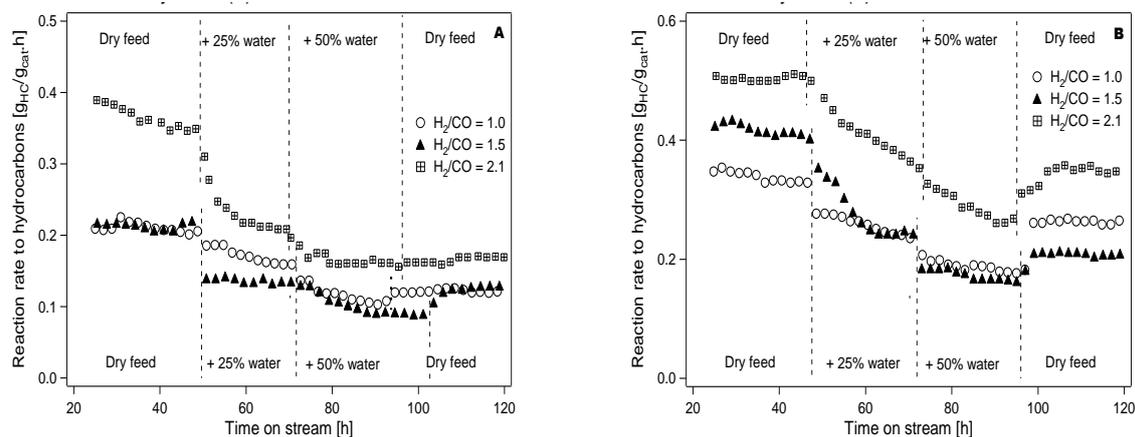


Fig. 1. Reaction rate to hydrocarbons as a function of time on stream for Co/Al₂O₃ (A) and CoRe/Al₂O₃ (B) $P_{Tot} = 20$ bar, $T = 483$ K.

The water addition also causes deactivation of the Co-Re/Al₂O₃ catalyst for all types of syngases as seen in Fig.1(B). The decrease of hydrogen formation rates on Co-Re/Al₂O₃ catalyst was more severe for syngas H₂/CO-ratio 1.0 and 1.5 than

syngas H₂/CO-ratio 2.1. However, in general the loss in activity and the rate of deactivation on Co-Re catalysts are less compare to that those for the Co un-promoted one. Adding about 20% water

(inlet $P_{H_2O} / P_{H_2} = 0.37$) to syngas H_2/CO -ratio 2.1 caused deactivation of Co/Al_2O_3 and $Co-Re/Al_2O_3$ over a period of 20 h by 37.4% and 19.9% of the initial activity respectively. This phenomenon was different with other study result [Storsæter *et.al.* 2005a] which is found the opposite; the $Co-Re/Al_2O_3$ was more severe deactivated by water than the Co compartment.

The reason was the $Co-Re/Al_2O_3$ catalyst has a higher dispersion so it will increase tendency to oxidize when it was exposed to the water [Kim 1993, Schulz *et.al.* 1994]. However, the reducibility of $Co-Re/Al_2O_3$ is higher too so it is still remaining a question which one is more affected to the activity. On the other hand, Kim (1993) reported increased activity for Re promoted and un-promoted Co/TiO_2 catalysts. Another result, Li *et.al.* (2002b) found that water decreased CO conversion of a Co/TiO_2 catalyst. An explanation that has been offered [Li *et.al.* 2002a, Storsæter *et.al.* 2005a] is the water possibly destroyed the strong metal-support interaction effect for both Co catalysts on Al_2O_3 and TiO_2 . From the comparison among three syngases and two catalysts, the conversion to hydrocarbons with the addition of water for syngas with H_2/CO -ratio 1.0 for both catalysts were the highest value. After water was stopped from the feed, some part of the activity lost during water addition was recovered except for the ratio inlet 2.1 on catalyst Co/Al_2O_3 . For the syngas H_2/CO -ratio 1.0 on $Co-Re/Al_2O_3$ the activity of catalyst returned back to the condition when 20% water was added. However for the two other H_2/CO -ratio inlets the activity of catalyst were not able to reach any condition before the 33% water co-feeding. It just a small of the activity is recovered. Even for syngas H_2/CO -ratio 2.1 on catalyst Co/Al_2O_3 the catalyst deactivation seems to be permanent. This is not in compliance with previous study [Hilmen *et.al.* 1999, Storsæter *et.al.* 2005a]. In those studies,

even though they used ratio inlet 2.1 the activity was regain to the value when the 20% water was added. However, it has been previously reported that the deactivation occurring at high conversions or at high water partial pressures is irreversible [Storsæter *et.al.* 2005a, Huber *et.al.* 2001].

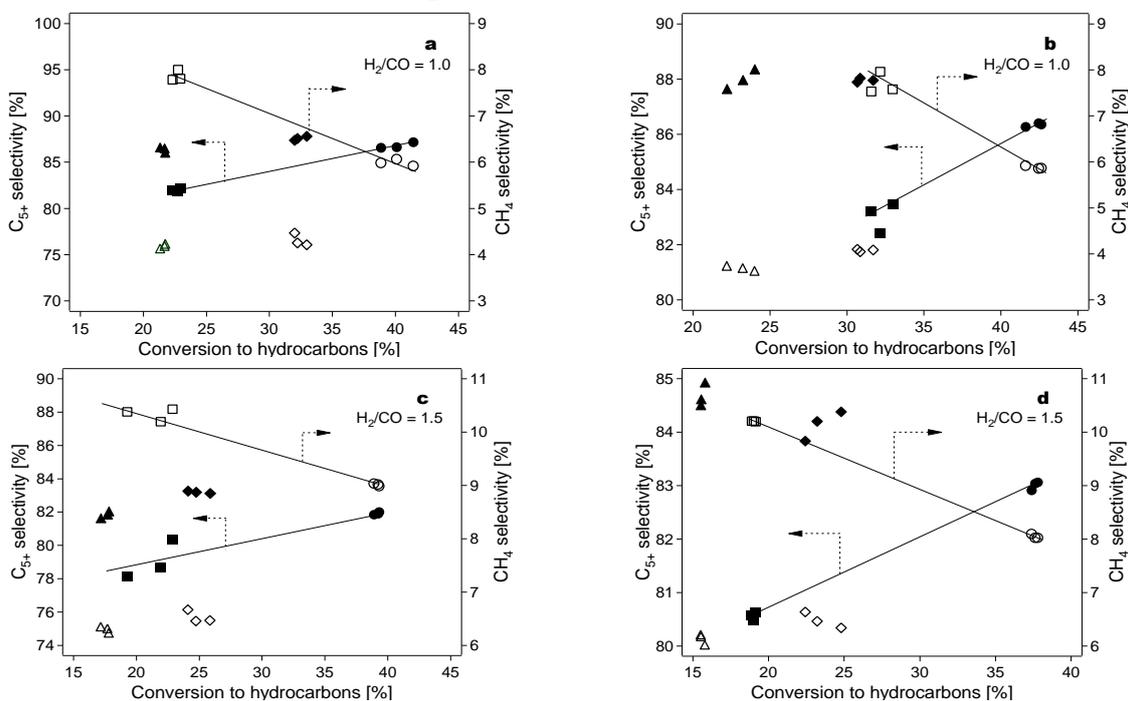
From our previous study [Tristantini *et.al.* 2006] we proved that the more hydrogen in the feed gas, the higher selectivity to CH_4 achieved and the lower selectivity to C_{5+} as complement. This results is in accordance with van Der Laan and Beenackers's (1999). Many studies of the effect of water addition to C_{5+} selectivity and CH_4 selectivity were addressed to cobalt supported catalysts. The result of water addition in the increase of selectivity to C_{5+} and decrease of selectivity to CH_4 were proved on Co/SiO_2 [Zowtiak *et.al.* 1983], Co/TiO_2 [Li *et.al.* 2002b], Co/Al_2O_3 and $Co-Re/Al_2O_3$ [Hilmen *et.al.* 1999, Storsæter *et.al.* 2005a]. Fig.2 shows the selectivity to C_{5+} and selectivity to CH_4 as a function of the conversion to hydrocarbon at different conditions for Co/Al_2O_3 (a, c and e) and $Co-Re/Al_2O_3$ (b, d and f) respectively. In dry conditions (before and after water addition) our result indicates that the selectivity to C_{5+} increases and selectivity to CH_4 decreases as conversion to hydrocarbon increases. This phenomenon employs for both catalysts and all types inlet ratio of syngases. The selectivity to C_{5+} increases and the selectivity to CH_4 decreases further (as conversion to hydrocarbon increases) by the addition of water for Co/Al_2O_3 catalyst and all type inlet of syngases. According to simplification of FTS reactions scheme [Storsæter *et.al.* 2005a], the reason is a lower rate of secondary hydrogenation and chain termination via hydrogen addition in the presence of water which indicate a lower availability of adsorbed hydrogen on the active Co surface. For $Co-Re/Al_2O_3$ the water co-feeding increases the C_{5+}

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selectivity only for ratio inlet 1.0 and it decreases the selectivity to C₅₊ for the other ratio inlets. In line with other studies, the increase of selectivity to C₅₊ by water addition was obtained for different Co-supported catalysts [Hilmen *et.al.* 1999, Krishnamoorthy *et.al.* 2002, Storsæter *et.al.* 2005b, Ekstrom and Lapszewicz 1986]. After water was stopped the selectivity to CH₄ increased to the higher value than the dry one. The same results on Co/TiO₂ for syngas ratio 2.1 was found in [Krishnamoorthy *et.al.* 2002]. For all inlet ratios the selectivity to C₅₊ increases in the first water addition, but then the 33% water addition give different results to each ratio syngas on each catalyst. For the ratio inlets 1.0 and 1.5 on Co/Al₂O₃ the 33% water

decreases the selectivity to C₅₊ while on Co-Re/Al₂O₃ it does not change the C₅₊ selectivity. For the inlet ratio 2.1 on Co/Al₂O₃ the 33% water addition increases the selectivity to C₅₊ a little bit while on Co-Re/Al₂O₃ it does not give any effect. After water co-feeding was stopped, C₅₊ selectivity for ratio inlets 1.0 and 1.5 on Co/Al₂O₃ decrease back to a lower value than the C₅₊ selectivity prior the water co-feeding; while for the H₂/CO-ratio=2.1 the selectivity to C₅₊ decreases quite much lower than those in previous dry feed. It seems that the negative effect of water to the C₅₊ selectivity for the ratio syngas 2.1 on both catalysts were more severe than the same effect to the ratio syngas 1.0 and 1.5.

Effect of water addition and inlet H₂/CO-ratios on the WGS-activities



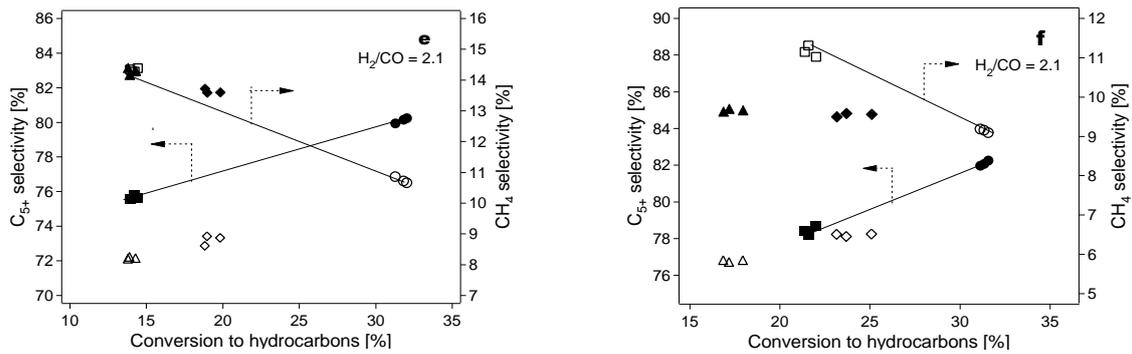


Fig. 2. C_{5+} selectivity (filled symbols) and CH_4 selectivity (open symbols) as a function of conversion to hydrocarbons at different conditions for Co/Al_2O_3 (a, c and e) and $Co-Re/Al_2O_3$ (b, d and f). Before water addition (o, ●), + 20% water (◇, ◆), + 33% water (Δ, ▲), and after water addition (■, □), $P_{Tot} = 20$ bar, $T = 483$ K.

To investigate one of the WGS-activities we assumed that the conversion of CO to CO_2 can be taken as the contribution of the shift reaction only [Ekstrom and Lapszewicz 198]. As we reported in our previous study [Tristantini *et.al.*2006], the decrease of H_2/CO -ratios in the feed resulted in an increase of the selectivity to CO_2 . In general the selectivity to CO_2 for Co/Al_2O_3 catalyst was higher than that for catalyst $Co-Re/Al_2O_3$. The reason found is that Re promotes the reduction of highly dispersed cobalt oxide interacting with support, thereby increasing the degree of reduction [Storsæter *et.al.* 2005a]. The water co-feeding increases the selectivity to CO_2 for all type of H_2/CO -ratio inlets and for both catalysts as shown in Fig. 3. The more water added the higher selectivity to CO_2 reached. The increase could be understood due to water seems increases the WGS activity just as (1.2). The selectivity to CO_2 in the periods with the exist of water for the H_2/CO -ratio = 1 on Co/Al_2O_3 is the highest values compare to other ratios inlets in the same periods. This is probably due to the $\frac{p_{H_2O}}{p_{H_2}}$ in the feed gas of H_2/CO -ratios = 1 is the highest one. This result is in agreement with Ekstrom and Lapszewicz (1986) who suggested that feed gases with any H_2/CO -ratio can be processed, provided that sufficient H_2O is added to give the required

amount of H_2 via the WGS. However, they found that the selectivity to CO_2 was not a function of the hydrogen concentration in the feed. The reason was the FTS rate is faster than the WGS rate. Another effect of the water addition to the WGS activity appears in the usage ratio. Fig. 4 shows the usage ratio at different periods (conditions) in experiment. The usage ratio is the ratio of H_2 to CO consumed in the FT synthesis based on the product selectivity to hydrocarbons minus the selectivity to CO_2 . Therefore for similar product of reactions, if the selectivity to CO_2 is higher it will result a lower usage ratio due to the assumption that the CO_2 is produced merely from WGS reaction. In the case of FTS with three different H_2/CO -ratio inlets, the usage ratio decreases insignificantly by water addition. The decrease of usage ratio is a little bit more when the water added was increased. After water is stopped the usage ratio increases back to the same value in dry condition. The usage ratio for the H_2/CO -ratio of syngases of 1.0 and 1.5 were slightly lower than this for H_2/CO -ratio 2.1. However, it is proved that the WGS occurs a little bit higher for these two syngases compare to that this for H_2/CO -ratio of 2.1 syngas. If we keep in mind that the $\frac{p_{H_2O}}{p_{H_2}}$ is higher in H_2/CO -ratio=1 and 1.5 syngases so this result could be partly in agreement with

Ekstrom and Lapszewicz's (1986) results again. In their study using Co/MgO/ThO₂/kieselguhr catalyst, they claimed that the usage ratio was independent of the H_2/CO -ratio in which sufficient water was added to the feed gas. The highest selectivity to CO_2 and the lowest usage ratio was found for the un-promoted Co-catalyst at the lowest inlet H_2/CO -ratio (1.0). When the co-feeding water is doubled the selectivity to CO_2 increases from 2.5 % to 3.77 % and the usage ratio decreases from 1.97 to 1.93. However, this result is only marginal compared to the dry feed result in spite of the large amount of steam present (25 % and 33%). Interestingly, after water was removed, for

Co and Co-Re catalysts and for all type of syngases, the selectivity to CO_2 is still higher than its value in the dry feed (period 2). This means that water changed the catalyst performance which is initially not so active in WGS to become more active one and the change is partly remain although the water has been removed. If the increasing of the selectivity to CO_2 caused by deactivation of the catalyst; thus deactivation which lead to CO_2 formation is only partly reversible. The deactivation is probably in relation with the re-oxidation of metallic cobalt [Krishnamoorthy *et.al.* 2002, Schanke *et.al.* 1995, Zhang *et.al.* 1999].

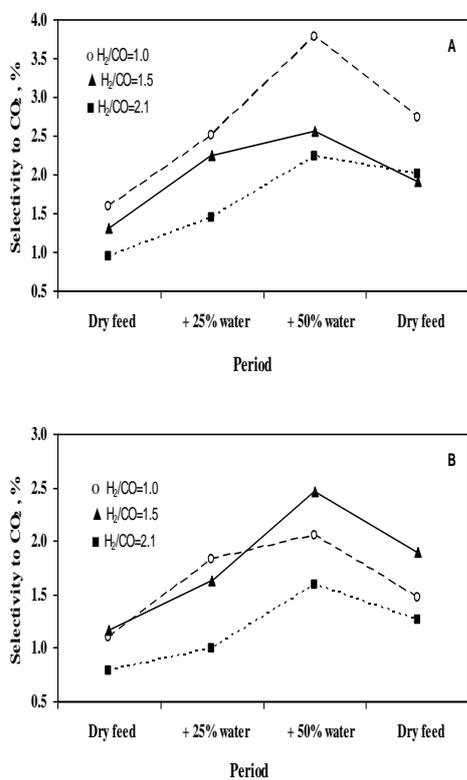


Fig. 3. Selectivity to CO_2 at different periods in experiment for Co/Al₂O₃ (A) and CoRe/Al₂O₃ (B) $P_{Tot} = 20$ bar, $T = 483$ K.

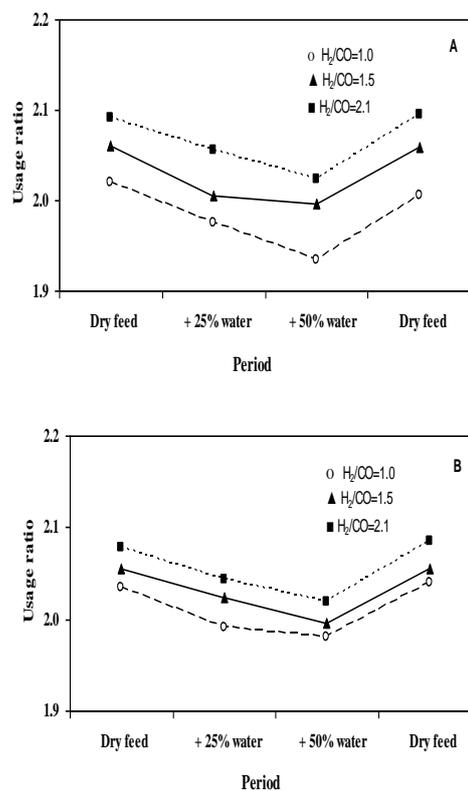


Fig. 4. Usage ratio at different periods in experiment for Co/Al₂O₃ (A) and CoRe/Al₂O₃ (B) $P_{Tot} = 20$ bar, $T = 483$ K.

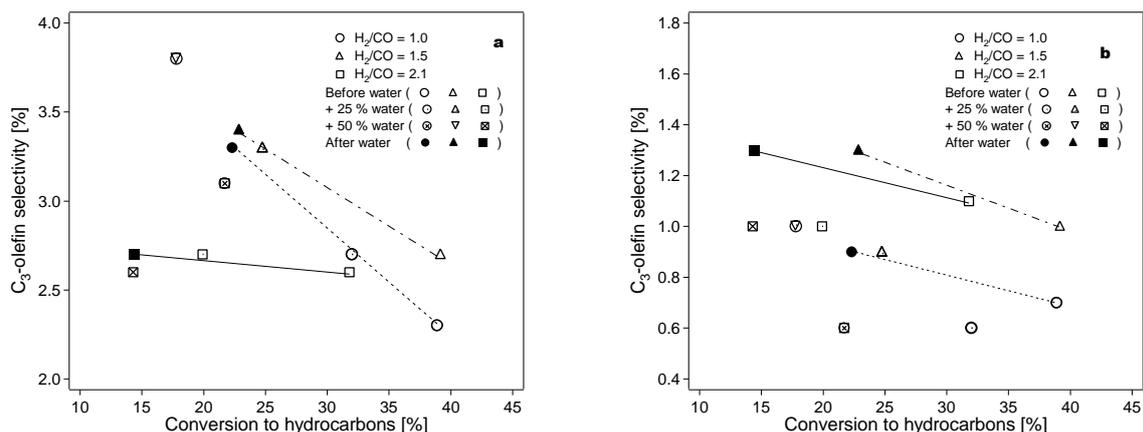


Fig. 5. C₃-olefin (a) and paraffin selectivity (b) as a function of conversion to hydrocarbons before, during and after water addition for Co/Al₂O₃, $P_{Tot} = 20$ bar, $T = 483$ K.

Effect of water on olefin and paraffin selectivities and olefin/paraffin ratios

Selectivity to olefin and paraffin is influenced by process conditions and whether water is present or not. The C₃-olefin selectivity and C₃-paraffin selectivity for Co/Al₂O₃ under dry condition, at different level water additions and after water removal is presented in Fig. 5 (a and b). As shown in Fig. 5 (a) the propene selectivity for Co/Al₂O₃ decreases as the conversion is increased and it is affected by water addition. The water addition increases the propene selectivity for all H₂/CO-ratio inlets and for both catalysts. The decrease in olefin selectivity as the conversion is increased is due to the higher extent of α -olefin readsorption at higher residence times. Therefore this effect is more pronounced for the ratio inlets 1.0 and 1.5. This is in accordance with previous studies [Krishnamoorthy *et.al.* 2002, Storsæter *et.al.* 2005a]. However, after water was removed the decreased effect of propene selectivity is remained even it increases the propene selectivity further. This is not in a line with Storsæter *et.al.*'s (2005a) for similar catalyst and for Co/SiO₂ and Co/TiO₂. For all of inlet syngases the C₃-(olefin/paraffin)-ratio is smaller for the Co-Re/Al₂O₃ than for the Co/Al₂O₃. In contrast the C₅₊ selectivity is higher for Co-Re/Al₂O₃ for all inlet syngases. This is in agreement with previous study using 2.1 ratio inlet [Storsæter *et.al.* 2005a].

From Fig. 5 (b) it can be seen that the paraffin selectivity also decreases as conversion is increased but the decrease is not as much as the decrease in olefin selectivity. According to Aaserud *et.al.* (2004), the decrease in paraffin selectivity when water added is due to a lower rate of secondary hydrogenation and a lower rate of chain termination via hydrogen addition [Iglesia 1997]. Another explanation [Storsæter *et.al.* 2005a] it could be that water influences the probability of chain growth (i.e., through inhibition of the termination reaction). The consistency is the C₃ total selectivity decreases as the conversion is increased and it increases when the water is added (conversion is decreased). It is a little bit different from Storsæter *et.al.* (2005a) for Co/Al₂O₃ which the C₃ total selectivity is about unchanged as the conversion is increased. Nevertheless in general those results is still in agreement with [Storsæter *et.al.* 2005a] due to the C₃-(olefin/paraffin)-ratio is increased when water is introduced to the feed which indicates a reduced of secondary hydrogenation of primary olefin.

CONCLUSION

The effect of water on the direct use of hydrogen poor syngases with H₂/CO-ratio 1.0, 1.5 and 2.1 for 12% Co/Al₂O₃ and 12%Co-0.5%Re/Al₂O₃ has been studied in a fixed bed reactor under condition $P_7 = 20$ bar

an T = 483 K. The water was obtained to have a deactivation effect to the activity and the selectivity of catalysts. The conversion to hydrocarbon and the rate of hydrocarbon formation were decreased and the selectivity to CO₂ was increased during addition of different amount of water for both catalysts and for all H₂/CO-ratio of syngases. The water addition lowered the usage ratio insignificantly for all type inlets and for both of catalysts. The water co-feeding increased the C₅₊ selectivity and decreased the CH₄ selectivity for Co/Al₂O₃ for all type of inlets, while for Co-Re/Al₂O₃ water affected positively only for H₂/CO-ratio 1.0 syngas and for H₂/CO- ratio 1.5 and 2.1 it gave negative effect. After water was stopped the activity for both of catalyst for the ratio inlet 1.0 and 1.5 was partly recovered but it was not for the 2.1 one. The Re-promoted catalyst was more active and selective for all H₂/CO-ratio of syngases.

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