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Process development of co-production of synthetic natural gas (Green SNG) and Fischer-Tropsch diesel

(Processutveckling av samtidig produktion av syntetisk naturgas (grön SNG) och Fischer-Tropsch diesel)

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"Catalyzing energygas development
for sustainable solutions"

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About SGC

SGC is a leading-edge company within the field of sustainable development having a national Swedish assignment. We work under the vision of *“Catalyzing energy gas development for sustainable solutions”*. We co-ordinate technical development including manufacture, distribution and utilization of energy gases and spread knowledge on energy gases. Focus is on renewable gases from anaerobic digestion and gasification. Together with private companies and the Swedish Energy Agency and its frame program *Development program for energy gas technology* we develop new solutions where the energy gases could provide benefits for a sustainable society. Together with our program committees within *Anaerobic digestion*, *Gasification and fuel synthesis*, *Distribution and storage*, *Power/Heat* and *Gaseous fuels* we identify issues of joint interest for the industry to build common research, development and/or demonstrations projects around. Decisions on any financial support from the Swedish Energy Agency are made by the external Beslutsnämnden within the framework of the current 090401–130331 program.

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Malmö, Sweden 2013

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Förord

Till projektet med titel ”Processutveckling av samtidig produktion av syntetisk naturgas (grön SNG) och Fischer-Tropsch diesel” har följande referensgrupp knutits:

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Projektet har bedrivits som ett doktorandarbete med civ. ing. Matteo Lualdi som doktorand. Handledare har varit docent Magali Boutonnet och professor Sven Järås. Projektet har bedrivits under tiden 2008-01-01 – 2012-09-15.

För en mer detaljerad rapport se Matteo Lualdis doktorsavhandling:

Matteo Lualdi, ”Fischer-Tropsch synthesis over Cobalt-based catalysts for BTL applications”, KTH, Doctoral Thesis in Chemical Engineering, Sept 2012.

Foreword

The following reference group has been created for the project titled “Process development of co-production of synthetic natural gas and Fischer-Tropsch diesel”:

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The project has been carried out as a PhD project with MSc. Matteo Lualdi as PhD candidate. Supervisors were Ass. Professor Magali Boutonnet and Professor Sven Järås.
The project has been carried out during the period 2008-01-01 - 2012-09-15.
For a more detailed report, see Matteo Lualdi´s Doctoral Thesis:

Matteo Lualdi, ”Fischer-Tropsch synthesis over Cobalt-based catalysts for BTL applications”, KTH, Doctoral Thesis in Chemical Engineering, Sept 2012.

Summary

The present study focuses on methanation and the Fischer-Tropsch synthesis (FTS) which are technologies that allow converting synthesis gas, a mixture of CO and H_2, into fuels. This technology has great potential for producing synthetic fuels from renewable sources, such as biomass, after its thermochemical conversion (gasification) into synthesis gas. In the methanation reaction, the synthesis gas is converted into methane and short-chain gaseous hydrocarbons while in the FTS a broad spectrum of products are formed, ranging from short-chain gaseous hydrocarbons (mostly methane) to very long ones (waxes).

The combination of these two processes can increase the energy efficiency and plant economy, since during FTS gaseous products are usually considered as a loss and these hydrocarbons are usually recycled to a reformer to be converted back into CO and H_2, while in this case they become desired products.

For the FTS, different cobalt-based catalysts have been tested and the effects of process parameters, such as a low H_2/CO ratio, typical of a biomass-derived synthesis gas, and water partial pressure have been studied.

Different catalysts for the methanation reaction were tested, with synthesis gas derived from biomass, focusing on the catalytic properties (activity, selectivity and catalyst life) and identifying the main deactivation causes as functions of operating conditions (temperature, pressure and composition); carbon formation was a focus of catalyst deactivation behavior.

Sammanfattning på svenska

Denna rapport avser ett projekt för samtidig produktion av syntetisk naturgas (green SNG) och Fischer-Tropsch-bränslen. Projektet bygger på att med utgångspunkt från syntesgas (CO + H_2 från förgasad biomassa) framställa SNG och syntetisk diesel i Sverige. Användningen av SNG utgör ungefär drygt 20% av konsumtionen av totala SNG plus diesel i Sverige. En studie av ECN i Holland har visat att för Holland kan effektiviteten öka med mer än 25% om SNG och diesel framställs i samma process jämfört med i två separata processer. Skillnaden mellan Holland och Sverige är andelen SNG av summan SNG + diesel som är drygt 20% för Sverige. Med ett metaniseringssteg direkt efter ett Fischer-Tropsch-steg kan den svenska marknadskvoten erhållas. I ett metaniseringssteg omvandlas CO och H_2 till metan och gasformiga korta kolkedjor medan i ett FT-steg omvandlas syntesgasen till ett brett spektrum av kolväten. I ett FT-steg kan man således erhålla allt från metan (CH_4) till vaxer (långa kolkedjor). Vaxerna kan sedan i ett separat steg hydrokrackas till diesel. I en separat FT-process betraktas de gasformiga produkterna som förlust och recirkuleras därför normalt till en reformer för att göra mer CO och H_2. Men om FT-processen följs direkt av ett metaniseringssteg kan således en mer än 25%-ig effektivisering erhållas.

I FT-processen har Co-baserade katalysatorer studerats. Processparametrar såsom en låg H_2/CO-kvot (erhålls normalt från förgasning av biomassa), vattentillsatser och olika specifika flöden har också studerats. Speciellt har en blandning av vattengasskiftkatalysator (WGS) och FT-katalysator studerats för att följa det interna vattengasskiftet ($CO + H_2O \rightarrow CO_2 + H_2$). Med intern WGS kan lägre H_2/CO-kvoter användas utan ett separat WGS-steg. Slutsatsen är att för Sverige kan den svenska marknadskvoten för SNG/(SNG + diesel) uppfyllas. En mindre ökning av SNG kan tillgodoses med processjusteringar medan en större SNG-andel kräver ett separat parallellt SNG-steg.

Vidare har metaniseringskatalysatorer (Ni) studerats. Aktivitet, selektivitet och katalysatorlivslängd har undersökts. Speciellt har deaktiveringsförloppet studerats. Med tiden deaktiveras katalysatorn. Orsakerna till detta är olika för olika bärarmaterial. Processparametrar som temperatur, tryck och gassammansättning har följts. Två typer av deaktivering kunde visas; dels agglomerering av den aktiva fasen till större kristalliter, dels kolbildning (olika typer av kol).

Som en slutlig sammanfattning har en kombination av en Co-baserad FT-katalysator och en Ni/TiO_2-baserad metaniseringskatalysator visat potential för en effektiv SNG- och dieselproduktion anpassad för svenska förhållanden. De studerade katalysatorerna har utvecklats av Kemisk Teknologi, KTH, inom ramen för projektet.

Innehåll

1. Background

Depletion of fossil energy sources is one of the important challenges that mankind will have to face in the coming years. Oil in particular, which has been the most important energy source in the 20th century, is expected to reach its production peak in the next few years, if it has not already been reached [1]. Furthermore, awareness of environmental issues caused by fossil fuel utilization has increased with the years. In fact, the use of fossil fuel through combustion is causing global and local environmental issues: on a global scale, the climate change resulting from anthropogenic greenhouse gas emissions (primarily CO_2) and, at local level, poisonous emissions such as SO_2, NOx and particulates. Therefore, an increasing energy demand, which would cause a fossil-fuel supply limitation with large economic impact, and the environmental problems are both driving forces for actions towards a more sustainable energy system. These actions include rationalization of energy consumption, increasing energy efficiency, use of lower carbon-content fuels (e.g. natural gas), CO_2 capture and storage, which could allow for the use of more abundant resources such as coal, and the use of renewable energy sources. Moreover, focusing the attention on energy consumption in the transportation sector, biomass and natural gas can play a role in the reduction of the oil share. No other renewable source but biomass can, at the moment, be directly utilized for this sector. These two issues make the conversion of biomass to fuels (liquid and gaseous) interesting processes.

The FTS is a polymerization reaction that produces a broad spectrum of products ranging from short-chain hydrocarbons (HC) such as methane to long chains such as waxes. The general reaction is as follows:

$$CO + 2H_2 \rightarrow \text{"-}CH_2\text{-"} + H_2O \quad \text{(eq. 1)}$$

The desired products of the FTS are hard waxes that would subsequently be converted into diesel fuel. The gaseous HC are usually considered a loss and are recycled to a reformer to be converted back into synthesis gas.

Moreover, according to a study performed by ECN [1], a more economical solution is to couple the production of synthetic diesel (via FTS) and synthetic natural gas (SNG) according to the so called “integrated co-production concept” in which the synthesis gas produced from a gasifier is fed, after conditioning and cleaning, to a FT reactor followed by a methanation reactor, as shown in Fig. 1.

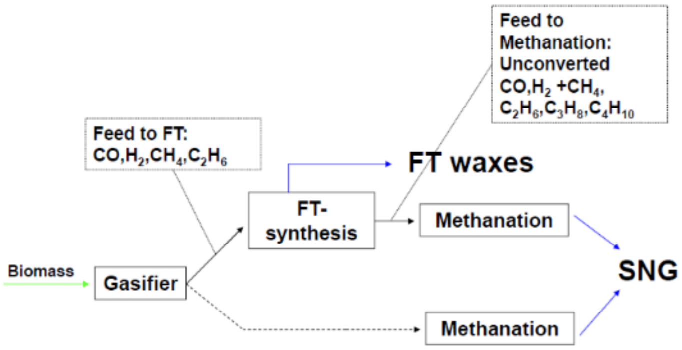


Figure 1. Integrated co-production concept [1].

The main advantage of the concept is that the off-gases from the FT reactor, composed of unreacted synthesis gas and the short-chain hydrocarbons produced in the synthesis, are not recycled to be converted back into synthesis gas but they become desired products. The difference between the ECN study and this study is mainly the Swedish market situation. Sweden consumes much less natural gas than Holland. This project has therefore focused on this difference.

Considering the Swedish energy market, in which the natural gas consumption is about 12 TWh/y and the diesel consumption around 47 TWh/y (varying slightly over the year), a conventional Fischer-Tropsch catalyst produces a ratio of gaseous HCs to liquid fuels resembling that of the Swedish market with about 22% C_1-C_4 HCs (energy based). If a different ratio is desired an extra methanation reactor is required.

THE OBJECTIVE OF THIS WORK is to optimize the SNG and diesel production in Sweden (from synthesis gas) through studying the effects of catalysts and process parameters. This means specially to study the low-temperature Fischer-Tropsch reaction parameters and their effect on product distribution and ratio between gaseous and wax products. The project also focuses on the catalyst ageing effects in the methanation step. More in detail, the work concerns Co-based catalysts used with a low H_2/CO-ratio syngas, typical of a biomass-derived syngas. Since water is the main product of the FTS and since cobalt catalysts have very poor water-gas shift (WGS) activity, the possibility of the direct use of H_2-poor syngas has been investigated by mechanically mixing a copper-based WGS catalyst and a cobalt-based FT catalyst in order to carry out internal shifting. This centers on the importance of water on both activity and selectivity to gaseous HCs as well as waxes. By performing internal shifting in the FT catalyst bed a separate WGS unit can be avoided increasing the efficiency of the process and reducing the investment costs.

Moreover, as concerns methanation over nickel-based catalysts, the work has been focused on the catalytic properties of methanation catalysts (activity, selectivity and especially catalyst life), identifying the main deactivation causes and the effects of operating conditions (temperature and reactant pressure) on catalyst deactivation, especially on carbon formation. Catalyst stability and life time are crucial factors for plant economy.

2. Experimental

Catalyst preparation

FT catalyst

The catalyst used in this study for Fischer-Tropsch synthesis consists of 12 wt. % Co supported on narrow-pore γ-Al_2O_3. The support was chosen since alumina is one of the most commercially used supports with high hydrothermal stability. The phases active for FT synthesis and used industrially are Fe and Co. The choice of Co was related to the fact that it can ensure higher conversion per pass compared to Fe.

Also, for comparison, as an example of the possibilities of catalyst development, a novel support was used to prepare a FT catalyst. The support used was SBA-15, a mesostructured support characterized by high hydrothermal stability and uniform pore size distribution.

WGS catalyst

A Cu-based water-gas shift catalyst was also prepared. A co-precipitated 30wt%Cu/30wt%ZnO/Al_2O_3 catalyst was prepared according to ref. [2]. Cu was chosen since it is the most used active phase for WGS at temperatures close to the ones of FT.

Methanation catalyst

Titania-supported and γ-alumina-supported nickel catalysts were prepared and tested in the methanation reaction. The Ni loading used for these catalysts was 20%, which is a typical value for a commercial catalyst. Just as for the FT catalyst, alumina was chosen as support because of its high hydrothermal stability and because the commercial methanation catalyst, produced by Topsøe, uses the same support type. Titania was instead chosen to increase the metal-support interaction as a means to prevent active-phase sintering.

Fischer-Tropsch synthesis

The Fischer-Tropsch (FT) synthesis was carried out in a down-flow stainless-steel fixed-bed reactor (i.d. 9 mm) with a loading of about 1 g Co catalyst (pellet size: 53 - 90 µm) mixed in different proportions with the WGS catalyst (pellet size: 53 - 90 µm) and diluted with 5 g SiC (average pellet size: 88 µm), resulting in a bed length of ~5-7 cm. The small pellet size used for the Co catalyst assures the absence of any mass-transfer limitations on the observed Co-catalyst-time yields. The different mechanical mixtures investigated were 0WGS-100FT, 15WGS-85FT, 33WGS-67FT and 50WGS-50FT, where the figures indicate wt.% of catalyst in the mixture.

The WGS reaction can be generalized as follows:

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (eq. 2)}$$

The process conditions used were 483 K, 20 bar and an inlet H_2/CO ratio of 1.0. The reactor tube was heated by means of an oven regulated by cascade temperature control with one sliding thermocouple in the catalyst bed and another placed in the oven. This system, together with an aluminum jacket placed outside the reactor, allowed for an even temperature profile in the catalyst bed (483 ± 0.8 K).

Prior to reaction, the Co-catalyst (or catalyst mixture) was activated in situ in pure H_2 (200 $Ncm^3/g_{Co\ cat}$, min) at atmospheric pressure at 493 K for 2 h (heating rate: 5 K/min). After activation, the reactor was cooled to 443 K and then flushed with He before increasing the pressure to the desired level. Then, the feed was switched to syngas, containing 3% N_2 as internal standard. Subsequently, the temperature was slowly increased to 483 K (rate = 0.15 K/min). The initial gas hourly space velocity (GHSV) was about 8200 $Ncm^3/g_{Co\ cat}$, h (period A) and held for approximately 24 h in order to reach a (pseudo) steady state condition. Then, the GHSV was lowered to ~1700-3300 $Ncm^3/g_{Co\ cat}$, h (period B) in order to increase the CO conversion and held for another 24 h.

The heavy HCs and most of the water were condensed in two consecutive traps kept at 393 K and room temperature, respectively. The product gases leaving the traps were depressurized and analyzed on-line by means of a gas chromatograph (GC) Agilent 6890 equipped with a TCD and a flame ionization detector (FID). H_2, N_2, CO, CH_4 and CO_2 were separated by a Carbosieve II packed column and analyzed on the TCD. C_1 – C_6 products were separated by an alumina-plot column and quantified on the FID allowing for determination of the C_{5+} selectivity (S_{C5+}). The CO_2-free S_{C5+} (i.e., S_{C5+} if excluding CO_2 from the C-atom balance) is defined as follows:

$$S_{C5+(CO2-free)} = 100 - (S_{C1} + S_{C2} + S_{C3} + S_{C4})_{(CO2-free)}$$

The reported HC selectivities are all C-atom based and CO_2 free. Aqueous products were analyzed off-line with a GC Agilent 6890 equipped with a FID and a capillary column (Hewlett-Packard HP-5). An internal standard (CH_3CN) was added to the aqueous phase prior to the injection.

The H_2/CO usage ratio (u.r.) is used as a measure of the relative WGS activity and defined as follows:

$$u.r. = \frac{3 \cdot S_{C1} + 2.1 \cdot S_{C2-C4} + 2 \cdot S_{C5+} - S_{CO2}}{100}$$

The lower the usage ratio, the higher the relative WGS activity. If all water produced in the FT reaction is used in WGS, the usage ratio is 0.5. For a process to be able to reach 100% syngas conversion (theoretically), the inlet H_2/CO ratio must equal the H_2/CO usage ratio.

Methanation Synthesis

The methanation synthesis was carried out in the same equipment as for the FT synthesis tests. The catalyst was mixed with SiC in order to dilute the catalyst. The catalyst was reduced in situ with a flow rate of 100 Nml/min of pure H_2. During the reduction the temperature was raised from ambient to 773 K at a rate of 5 K/min and subsequently kept constant during 9 h at 773 K. The procedure varied depending on the purpose of the experiment. Small amounts of catalyst (approximately 0.02 g and 1 cm bed) and large syngas flows (approximately 100 Nml/min), which were introduced into the reactor in a single step, were used to determine the initial activities in the different experiments. Making use of these operating conditions, the CO conversion level was low, and so the heat of reaction was easily removed by the aluminum jacketing and the large unreacted flow. The temperature did not increase significantly during the starting up of the operation (approximately 1 K). Unfortunately, no further characterization of the catalyst was possible with such small quantities, so a different procedure was performed if characterization was needed. A minimum of 0.1 g of catalyst was necessary for further characterization. When these larger amounts of catalyst were used, it was necessary to start the experiments with a stepwise increase of the syngas flow up to the desired level in order to prevent a large temperature increase in the catalyst bed due to the exothermicity of the reaction. The starting up lasted approximately 30 min, so it was not possible to measure initial activities.

The reaction products were analyzed by means of GC as for the FT products.

3. Results and discussion

Fischer-Tropsch activity results

The catalytic performances in period A (higher GSHV, lower conversion) and B (lower GHSV, higher conversion) are summarized in Table 1. As expected, by increasing the fraction of WGS catalyst in the mixture an increase in CO_2 selectivity (S_{CO2}) (see eq. 2) and a decrease in usage ratio is generally seen for both periods A and B. These two parameters are a measurement of the WGS activity of the mixture.

From Table 1 it can also be seen that there is no correlation between the fraction of WGS catalyst in the mixture and the HC selectivities. One would expect the S_{C5+} to decrease and S_{C1} to increase with increased WGS activity as the H_2/CO ratio in the reactor is higher [3] and the water partial pressure is lower [4]. It can be also noticed that the ratio between the selectivity to methane and S_{C5+} is lower compared to that of the Swedish energy market. The lower selectivity to short-chain HCs can be ascribed to the low H_2/CO ratio of the syngas feed.

The usage ratios show only a weak dependence on GHSV, being around 2 for the pure Co catalyst and about 0.65-0.75 for the WGS catalyst-rich mixtures. A usage ratio equal to the inlet ratio is the requirement for complete conversion of the syngas.

The addition of WGS activity which converts part of the CO into H_2 resulting in an increase in average partial pressure of H_2 and a decrease in average partial pressure of CO. A conventional kinetic expression for FT rate over Co catalysts is as follows:

$$r_{FT} = A \cdot P_{H2}^{a} \cdot P_{CO}^{-b}$$

The rate is positively influenced by an increased P_{H2} and negative affected by an increase P_{CO}. Interestingly, for these results an increased P_{H2} (and decreased P_{CO}) does not correspond to an increase in the Co catalyst-time yield (mol CO converted to HCs / $g_{Co\ cat}$, s) as predicted by traditional Co catalyst rate expressions, but instead to a decrease. This finding is in contrast to what has been reported by Chanenchuk et al. [5] for a slurry reactor. This fact is probably related to the fact that the conventional expression does not consider a term related to $P_{H2O.}$ In Fig. 2, a correlation between the average P_{H2O} inside the reactor and the Co-catalyst-time yield to HCs is shown, indicating that at the present process conditions water has a larger positive effect on the FT rate than has hydrogen.

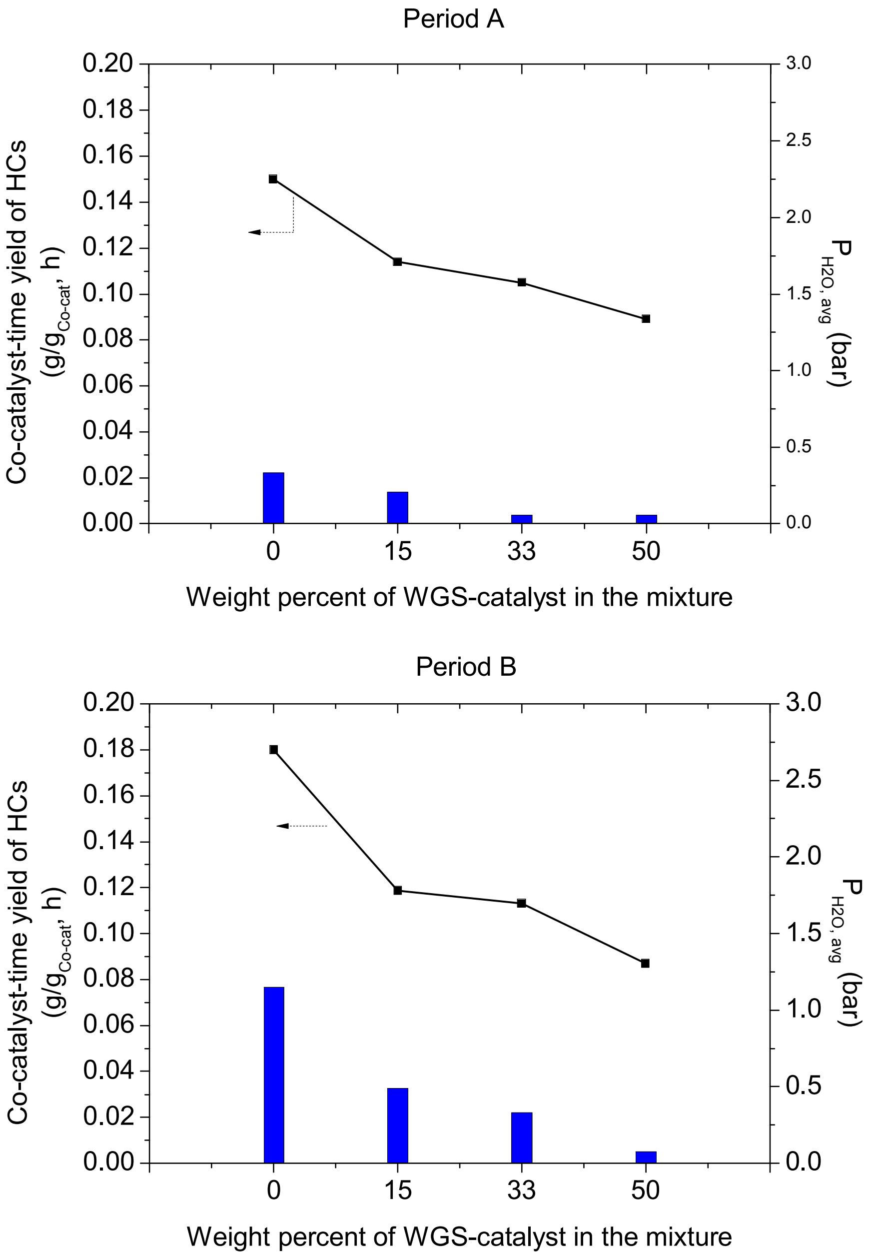


Figure 2. Co catalyst-time yields and reactor-average P_{H2O} vs. weight percent of WGS catalyst in the mixtures during periods A (upper) and B (lower). Experimental conditions: 483 K, 20 bar, H_2/CO = 1.0.

This has been reported to be due to olefins undergoing secondary hydrogenation over Cu-based catalysts [5], which seems as a reasonable explanation since the hydrogenation activity of the Co-catalyst, apparently, is invariant in the range of the studied process conditions. Since the used WGS catalyst is also a methanol synthesis catalyst, it is worth mentioning that the C atom selectivity to alcohols (in particular to methanol) was below 1% for all mixtures at the studied process conditions.

Table 1. Activity and selectivity data for periods A (left) and B (right). Experimental conditions: 483 K, 20 bar, inlet $H_2/CO = 1.0$. FT catalyst: 12% Co/Al_2O_3. WGS catalyst: $Cu/ZnO/Al_2O$.

[a] Selectivities are CO_2 free.

	Period A						**Period B**						
Sample	**GHSV (Ncm^3 / $g_{Co\text{-}cat}$, h)**	**X_{CO} (%)**	**Mol CO conv. to HCs * 10^6 (mol / $g_{Co.cat}$, s)**	**S_{CO2} (%)**	**S_{C1}[a] (%)**	**S_{C5+}[a] (%)**	**GHSV (Ncm^3 / $g_{Co\text{-}cat}$, h)**	**X_{CO} (%)**	**Mol CO conv. to HCs * 10^6 (mol / $g_{Co\text{-}cat}$, s)**	**S_{CO2} (%)**	**S_{C1}[a] (%)**	**S_{C5+}[a] (%)**	**u.r.**
0WGS-100FT	8000	6.5	2.95	0.8	6.0	87.3	3245	19.3	3.45	0.5	5.3	88.5	2.05
15WGS-85FT	8000	5.8	2.25	14.8	4.1	90.8	3280	15.2	2.33	18.8	6.2	86.7	1.49
33WGS-67FT	8000	8.0	2.06	43.2	5.2	88.8	1657	43.5	2.22	43.9	5.0	89.5	0.71
50WGS-50FT	8000	6.5	1.81	41.0	4.2	89.3	3309	17.3	1.72	45.6	5.0	88.1	0.65

On a pure Co catalyst supported on alumina the rate to HC was seen to increase upon external water addition only when the partial pressures of the reactant were kept constant. An increase in water partial pressure along the reactor corresponds to a typical effect of high conversion in industrial slurry reactors. When the water in the feed is increased, the selectivity to gaseous HCs decreases, especially to methane as shown in Fig. 3.

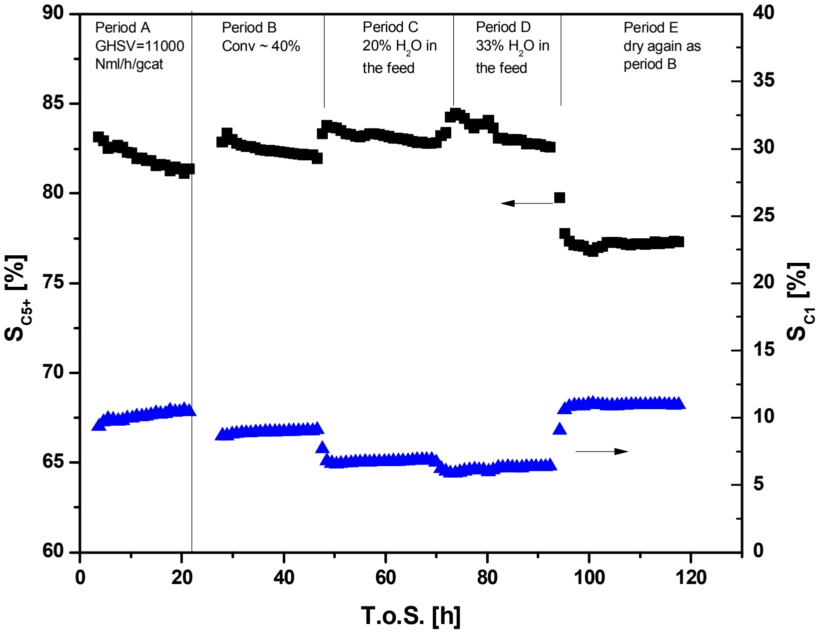


Figure 3. Effect of external water addition on the selectivities in FT over Co/Al_2O_3 Experimental conditions: 483 K, 20 bar, H_2/CO = 2.1.

Summarizing experimental data about the mixtures with the WGS catalyst where indigenous water is removed showed that no significant changes in product distribution but significant changes in the space-time yield to HCs. On the other hand, when larger amounts of water are co-fed to the reactor to simulate high conversion a significant inhibition of methane production is observed.

To give an example of other possibilities of catalyst development, Figure 3 shows a 12%Co on SBA-15 undergoing the same experimental sequence as for the catalyst shown in Figure 4. It can be seen that in the case of the 12%Co on SBA-15 catalyst, the selectivity to methane is higher in period A (high space velocity) and even more dependent on operating conditions such as conversion level and extent of water addition. It can be noticed that with a Co/Al_2O_3 catalyst, the ratio between SNG (C_1-C_4) and liquid HCs is similar to that of the Swedish market. A change in operating conditions such as an increase of temperature or H_2/CO ratio would result in an increase of the short-chain HC selectivities making possible a small adjustment of the ratio of SNG to liquid HCs.

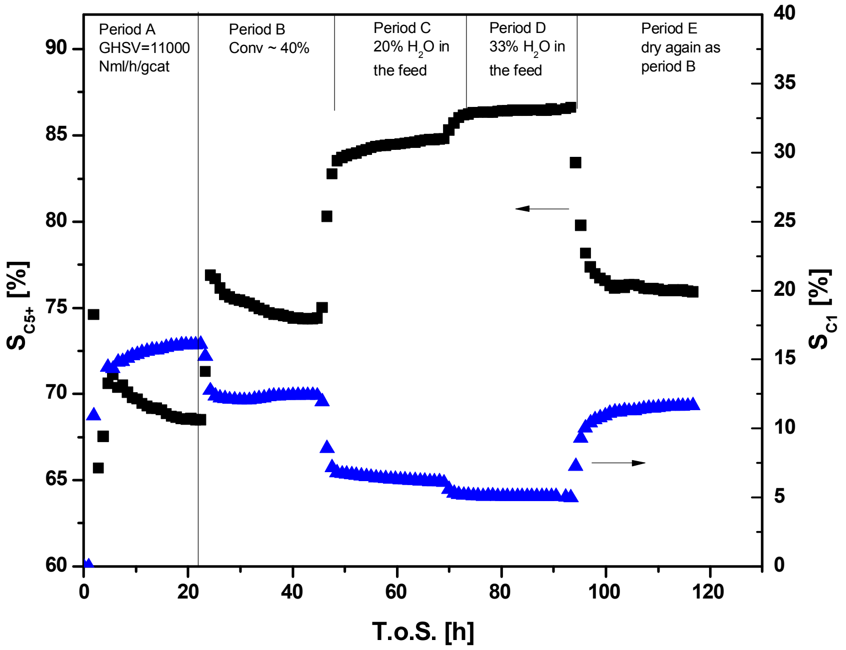


Figure 4. Effect of external water addition on the selectivities in FT over Co/SBA-15. Experimental conditions: 483 K, 20 bar, $H_2/CO = 2.1$.

Methanation activity results: comparison between Al_2O_3 and TiO_2 supports

The methanation experiments using the 20%Ni/TiO_2 catalysts differed from the one of 20%Ni/Al_2O_3. The overall initial activity was higher over alumina-supported than over titania-supported catalysts (see Figure 5), as expected, due to the difference in metal dispersion.

In agreement with other studies [6, 7], the results of these experiments also showed that the titania-supported nickel catalysts provide higher selectivity to longer chain hydrocarbons than alumina-supported (see Table 2).

These two differently supported nickel catalysts not only presented differences in their activity and selectivity but also in their deactivation behavior. While the alumina-supported catalysts gave a complete loss of activity the titania-supported ones showed a more stable behavior, in which the rate of deactivation slows down significantly after some hours on stream (see Figure 5).

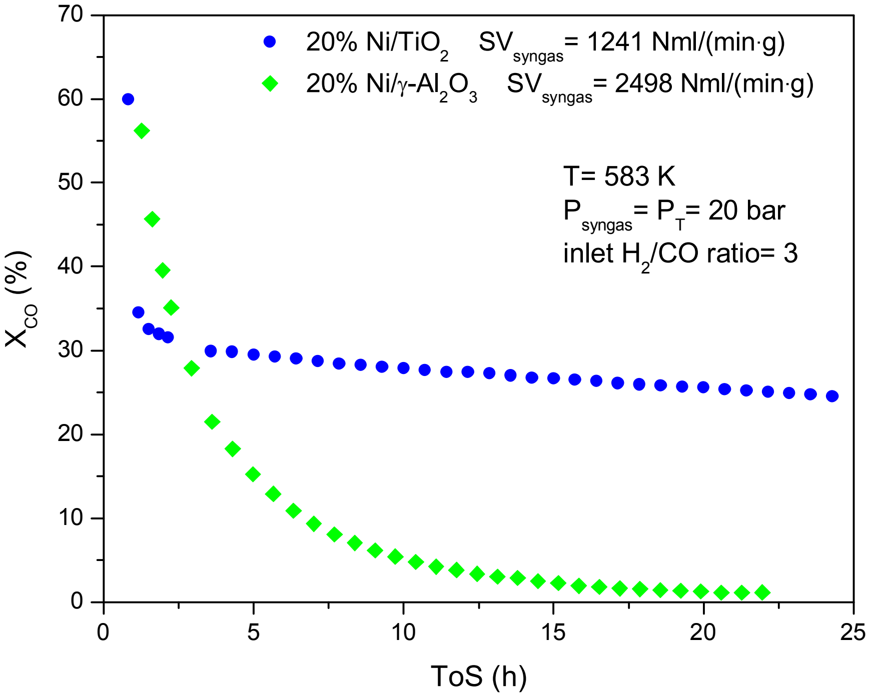


Figure 5: Deactivation on 20% Ni/TiO_2 and 20% Ni/Al_2O_3.

Table 2: Selectivities of titania and alumina-supported nickel catalysts after 5 h on stream.

Catalyst	**Selectivity (%)**		
	C_1	**C_2-C_4**	**C_{5+}**
20%Ni/TiO_2	50.2	38.8	11
20%Ni/Al_2O_3	58.1	35.5	6.4

Two possibilities have been investigated as causes for the deactivation behavior for these catalysts through X-ray diffraction (XRD) and Temperature Programmed Hydrogenation (TPH) (see also Appendix A). The former was used to investigate the active phase (nickel) particle size before and after reaction to validate the hypothesis of sintering as deactivation cause, the latter was use to quantify the amount of carbon formed and characterize the species of carbon present on the nickel surface.

Table 3: Nickel crystallite size for Ni/TiO_2 and Ni/Al_2O_3

Sample	**Fresh catalyst D_{Ni} (nm)**	**Spent catalyst D_{Ni} (nm)**
20% Ni/Al_2O_3	9	82
20% Ni/TiO_2	24	35

The results from XRD investigations are presented in Table 3. The results obtained show that the main reason for deactivation on Ni/Al_2O_3 is sintering of the active-phase particles.

On the other hand, the Ni/TiO_2 did not present such a significant particle growth which leads to the conclusion that the main reason for deactivation of this catalyst is probably carbon formation.

The catalysts were exposed to methanation conditions after TPH in order to see if the removal of carbon resulted in a recovery of activity.

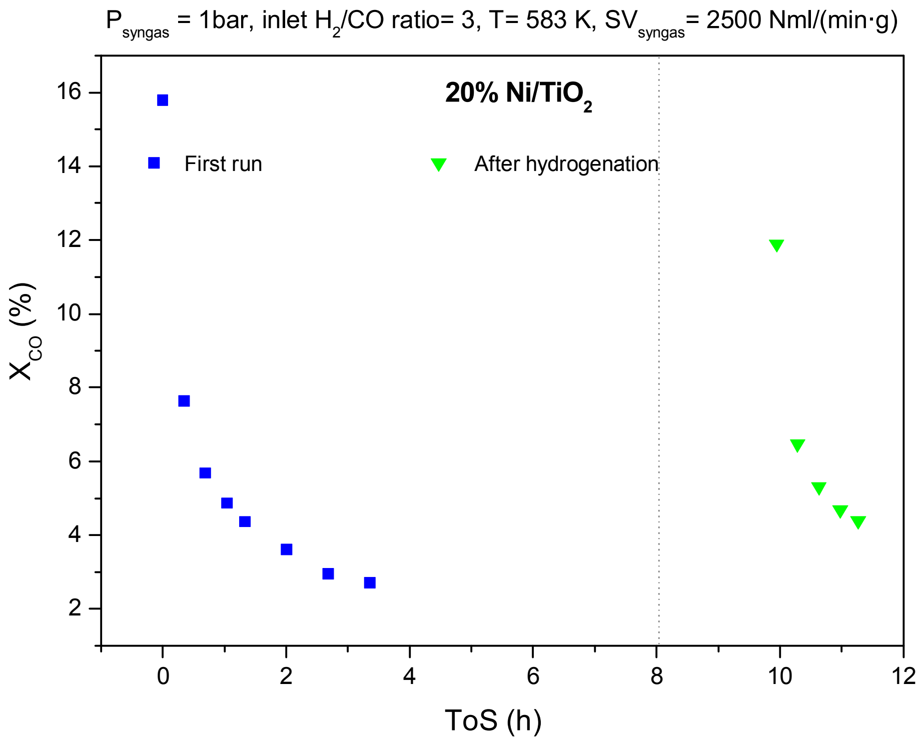


Figure 6: Effect of regeneration on 20% Ni/TiO_2.

The results showed an 80% recovery of activity after TPH, which demonstrates that the main reason for deactivation for Ni/TiO_2 was carbon formation (see Fig. 6).

The same procedure was applied on the 20% Ni/Al_2O_3 (see Fig. 7) to validate the conclusion drawn from XRD measurements. In contrast to the titania-supported catalyst, the alumina-supported did not show any recovery of activity after TPH, confirming the main cause of deactivation for the alumina-supported catalyst to be sintering.

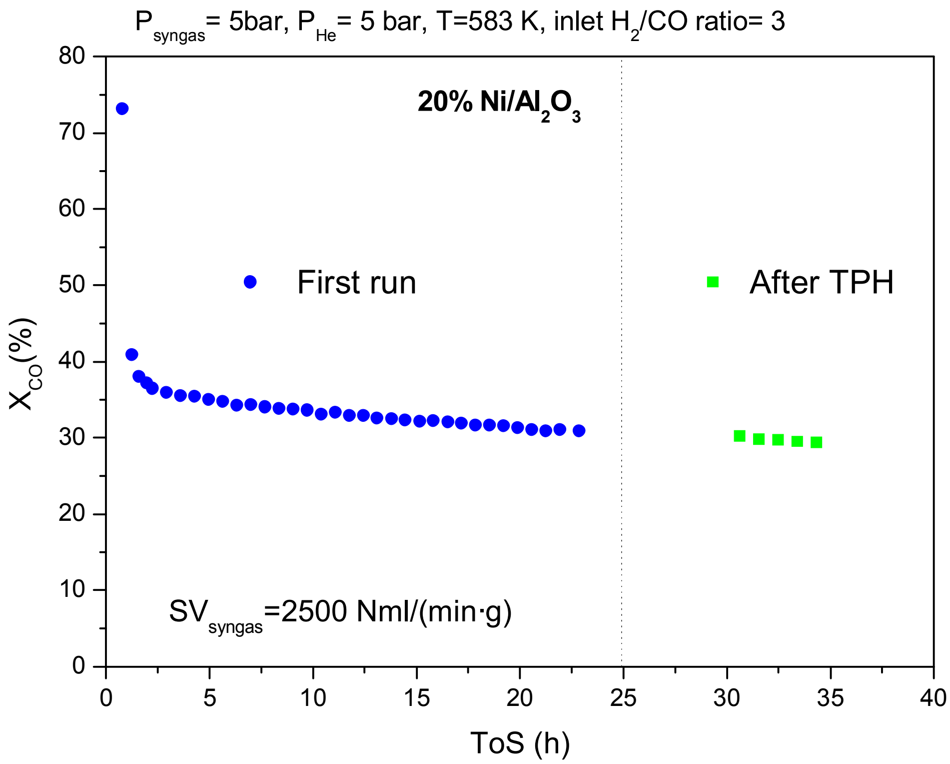


Figure 7: Regeneration on 20% Ni/Al_2O_3

Deactivation and carbon formation for 20%Ni/TiO_2 as function of process conditions.

Effect of H_2/CO ratio

The effect of H_2/CO ratio on the deactivation behavior and carbon formation was studied for the Ni/TiO_2 catalyst. Four experiments with different inlet H_2/CO ratios (2, 3, 6 and 9) were designed to start from the same conversion value (around 16%).

The experiments differed in their rate of deactivation (see Figure 8). The lower the initial H_2/CO ratio, the faster the deactivation of the catalyst.

The results obtained from TPH of these samples are presented in Figure 9 showing a clear correlation between the rate of deactivation and the amount of carbon accumulating on the surface.

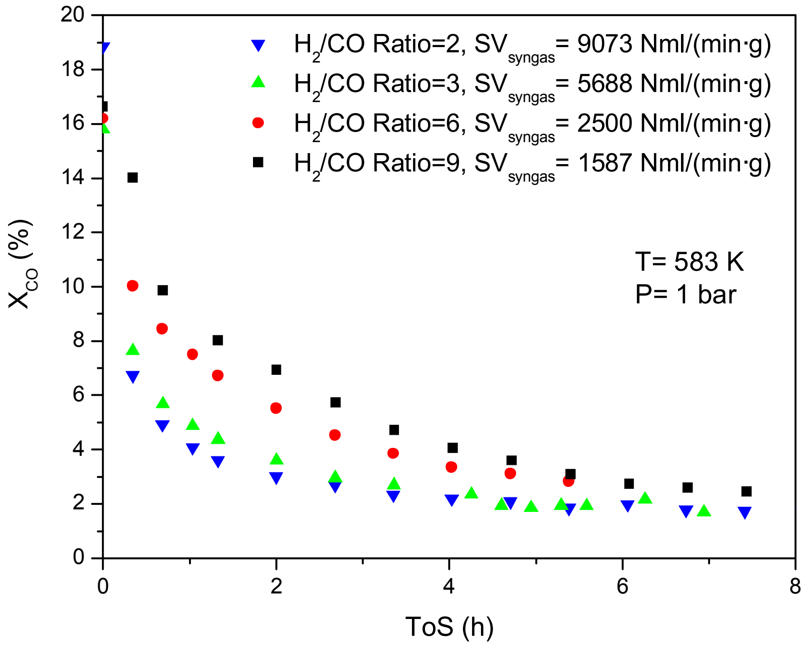


Figure 8: Effect of H_2/CO ratio on deactivation

The amount of carbon formed for all experiments during these 6 hours on stream could be enough to cover the entire nickel surface.

According to Bartholomew [7] the only carbon species that can be formed are $C_α$, $C_β$, and C_v, whose hydrogenation peak temperatures are 473, 673 and 673-873 K, respectively. This leads to the conclusion that, probably, the first peak corresponds to $C_α$. A possible explanation for the fact that this first peak changes in its hydrogenating temperature is that the nature of this carbon is an intermediate between $C_α$ and $C_β$, from monoatomic to polymeric carbon. It is still uncertain which species correspond to the other peaks but three peaks can be observed in the experiment with inlet H_2/CO ratio 6, so three carbon species are probably present.

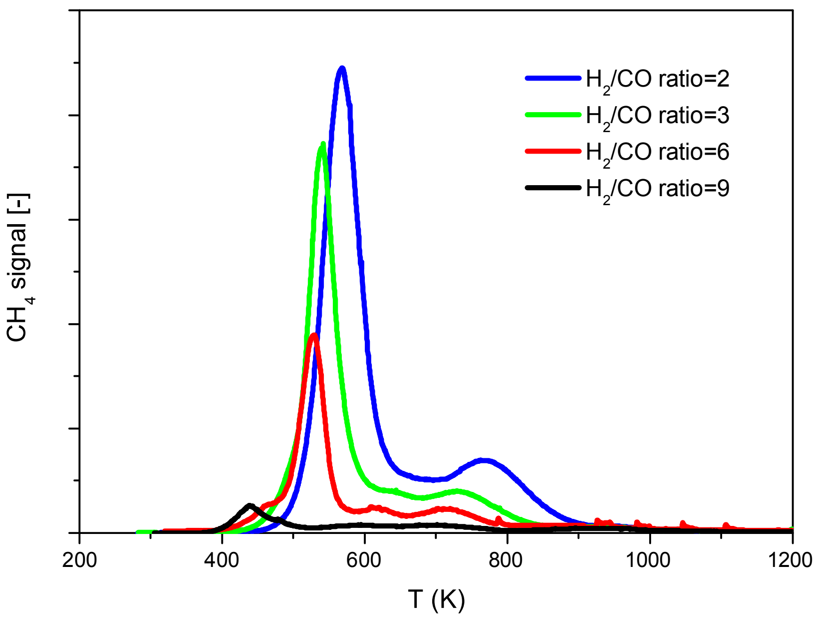


Figure 9: Effect of H_2/CO ratio on carbon formation (measure as methane signal)

Effect of temperature

Three experiments on methanation reactions at three different temperatures, 553, 583 and 613 K, were carried out at atmospheric pressure in order to investigate the effects of temperature on deactivation and carbon formation. In fact, a typical methanation reactor is an adiabatic fixed bed reactor in which the temperature increases along the bed length.

From Figure 10 it can be noticed that the higher the temperature of reaction the faster the loss of activity during the first hours on stream.

After 6 hours of operation, the reaction was stopped and a TPH was performed. The results from TPH are presented in Figure 11. The amount of carbon formed in all three experiments is likely to be enough to deactivate the catalyst completely.

The results do not present a significant difference between the experiments performed at 553 and 583 K. However, deactivation is much faster for the experiment carried out at 613 K and larger amounts of carbon deposits are found.

It can be noticed that the amount of carbon reduction between 700 and 900 K was larger at higher operating temperature. Therefore, the effect of temperature on the deactivation behavior seems to be related to the amount of hard-to-reduce carbon species, which according to Bartholomew [7] could be C_β and/or Cv. In contrast to the H_2/CO ratio, temperature does not affect in the hydrogenating temperature of the first peak.

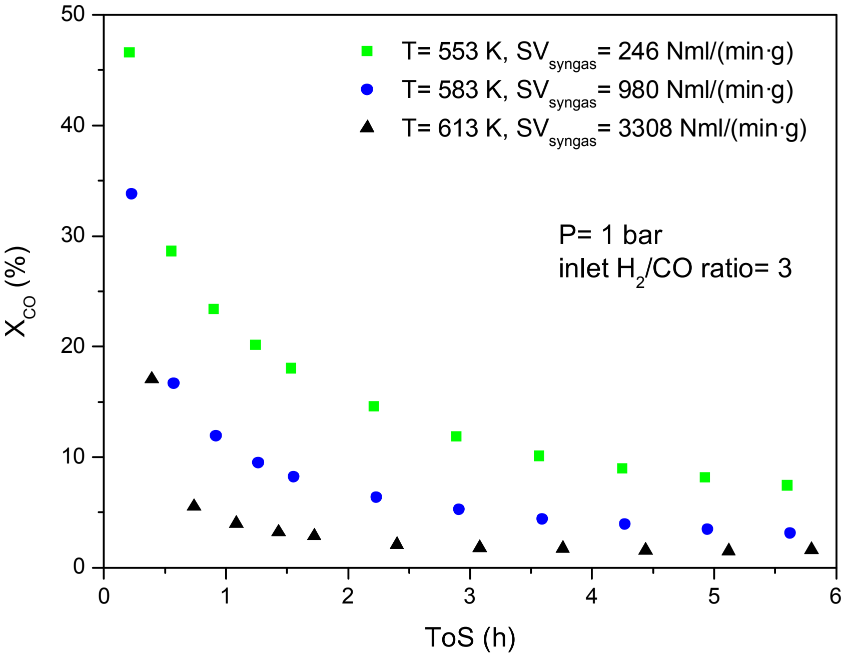


Figure 10: Effect of temperature on deactivation

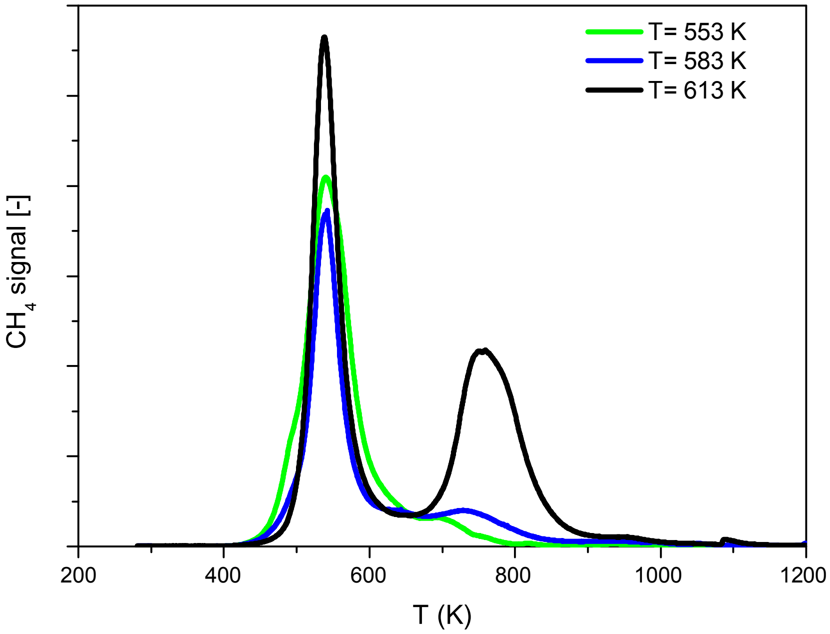


Figure 11: Effect of temperature on carbon formation (measured as methane signal)

<u>Effect of reactant pressure</u>

The data obtained in the previous sections offer interesting information about how the relation between H_2 and CO pressures affected deactivation and carbon formation at atmospheric pressure. However, it is necessary to study the same effect at higher pressure, closer to the industrial operating conditions.

In this section, the results of three experiments at a total pressure of 20 bar at the inlet H_2/CO ratios 2, 3 and 6 are presented. The H_2/CO ratio had the same effect at 20 bar as at atmospheric pressure. The lower the H_2/CO ratio, the faster the deactivation rate (see Figure 12).

In order to evaluate the effect of reactant pressure, it is necessary to compare the experiments at atmospheric pressure with the ones at 20 bar. The relative loss of activity of the experiments was higher at atmospheric pressure than at 20 bar (see Figure 13). Moreover, the amount of carbon formed at 20 bar was lower than at atmospheric pressure for the three inlet H_2/CO ratios studied.

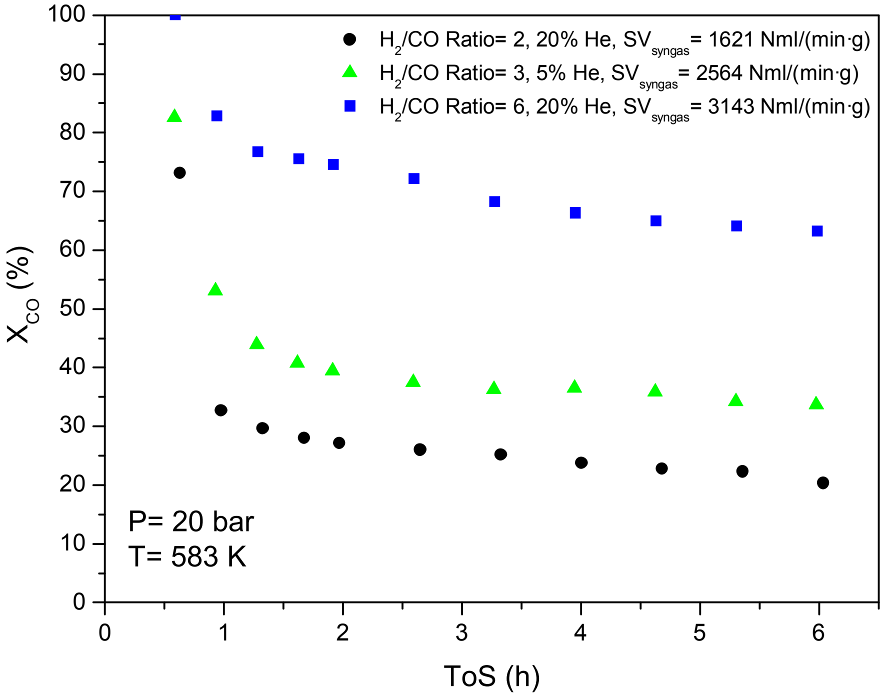
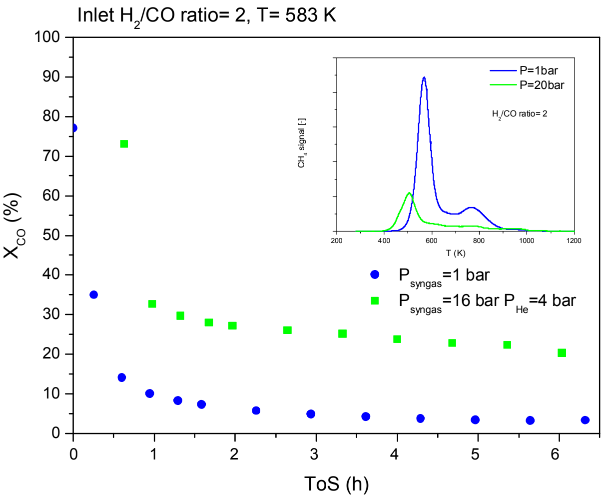
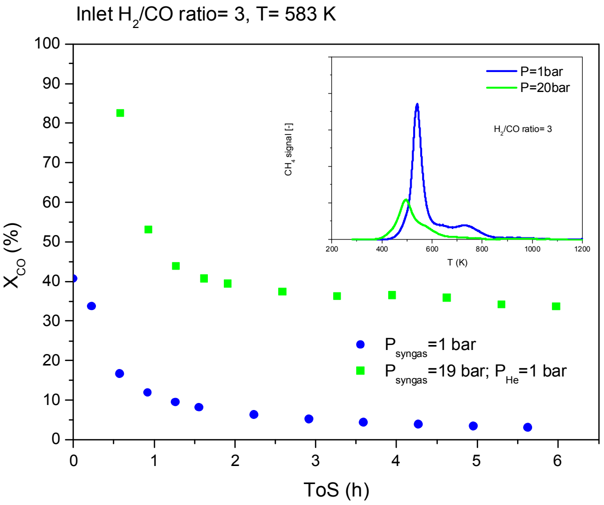


Figure 12: Effect of H_2/CO ratio on deactivation at 20 bar


Inlet H_2/CO ratio= 2, T= 583 K
X_{CO} (%)
ToS (h)
P=1bar
P=20bar
H_2/CO ratio= 2
CH_4 signal [-]
T (K)
P_{syngas}=1 bar
P_{syngas}=16 bar P_{He}=4 bar


Inlet H_2/CO ratio= 3, T= 583 K
X_{CO} (%)
ToS (h)
P=1bar
P=20bar
H_2/CO ratio= 3
CH_4 signal [-]
T (K)
P_{syngas}=1 bar
P_{syngas}=19 bar; P_{He}=1 bar

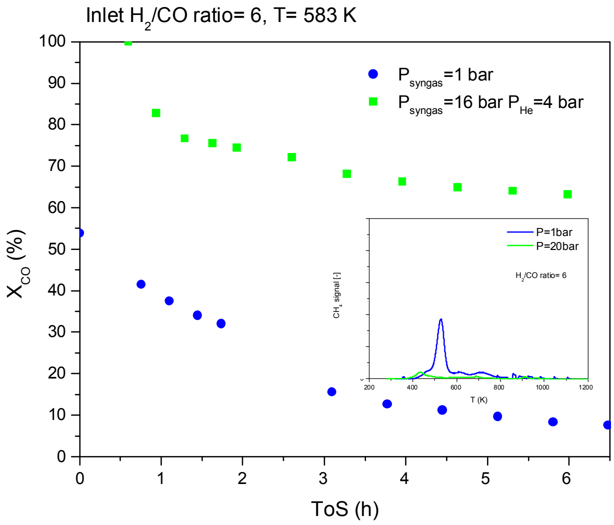


Figure 13: Effect of reactant pressure at different inlet H_2/CO ratios.

4. Conclusions and outlooks

Overall

The catalysts Co/Al_2O_3 and Ni/TiO_2 prepared and tested in this study could be used in commercial reactors. However, it is difficult to compare performances for commercial catalysts which have not been tested under the same conditions.

The results from this study also show that it is possible to obtain around 20-22% SNG with only a FT reactor. For small changes of this percentage, the amount of C_1-C_4 can be adjusted by changing process parameters in the FTS, such as higher temperature or increased inlet H_2/CO ratio, while for large changes a methanation reaction is required.

Fischer-Tropsch

A narrow-pore Co/γ-Al_2O_3 catalyst was mixed in different proportions with a WGS catalyst in a fixed-bed reactor with the initial intention to increase the production rate of HCs by increasing the partial pressure of hydrogen and decreasing that of CO inside the reactor. The usage H_2/CO ratio could be adjusted to match the inlet H_2/CO ratio of 1.0 by choosing the correct amounts of the two catalysts. However, the Co catalyst-time yields to HCs of the WGS catalyst-containing mixtures were lower than for the pure Co catalyst. Moreover, water which is one of the main products of the synthesis and whose concentration is related to the conversion level in the reactor (as well as the reactor of choice), showed a positive kinetic effect and inhibited methane formation, shifting the selectivity towards longer-chain HCs (organic liquid products and waxes). The nature of the water effect still remains unclear and requires further studies. In particular cases, it seems possible to replace a costly WGS unit and perform internal shifting in a FT reactor accepting a decrease of the rate to HC but a larger selectivity to C_{5+}.

Methanation

In this study it has been shown that, at the operating conditions used, the main reason for deactivation for titania-supported nickel catalysts is carbon formation while for alumina-supported catalysts it is sintering. Titania-supported nickel catalyst has a higher selectivity towards C_2, C_3 and C_4 hydrocarbons.

Furthermore, it was found that, for titania-supported nickel catalysts, the deactivation and thus the formation of carbon is enhanced at low H_2/CO ratios, high temperature and low reactant pressures. Further studies could focus on the quantification of the deactivation effects to relate catalyst life time and operating conditions to a kinetic expression for deactivation. On-line regeneration could be performed industrially to handle the type of deactivation which affects TiO_2. As catalyst replacement is a costly operation it seems important to follow up this finding with other projects.

5. Acknowledgements

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7. Appendix A: Characterization methods and results

Catalyst characterization methods

Brunauer-Emmet-Teller (BET) surface area and porosity measurements were performed in a Micromeritics ASAP 2000 unit. The samples were evacuated and dried at 523 K overnight prior to analysis. The BET area was estimated by N_2 adsorption at liquid nitrogen temperature at relative pressures between 0.06 and 0.2.

Hydrogen temperature-programmed-reduction (TPR) was used to study the reducibility of the catalyst. TPR of the calcined catalyst (0.15 g) was conducted in a Micromeritics Autochem 2910 flowing 5% H_2 in Ar increasing the temperature from ambient to 1200 K (10 K/min) while monitoring the H_2 consumption on a thermal conductivity detector (TCD). The degree of reduction (DOR, %) was estimated with H_2-TPR of the in-situ reduced catalysts. 0.15 g of calcined catalyst was reduced at 623 K (heating rate: 1 K/min) for 16 h in flowing H_2, then flushed with inert gas for 30 min. Afterwards, the flowing gas was changed to 5% H_2 in Ar and the temperature was increased from 623 to 1200 K (10 K/min) monitoring H_2 consumption. The TCD was calibrated with Ag_2O as standard.

In order to estimate the cobalt dispersion (D, %) and the cobalt crystallite size (d, nm), hydrogen static chemisorption was performed on the reduced catalysts. The chemisorption measurements were conducted on a Micromeritics ASAP 2020C unit at 308 K, after reducing about 0.15 g of the calcined catalysts in flowing hydrogen at 623 K (heating rate: 1 K/min) for 16 h. The average particle size of Co^0, assuming spherical shape, was estimated according to [3]:

$$d(Co^0)_H = \frac{96}{D} \cdot DOR$$

where DOR is the degree of reduction.

Wide angle X-ray diffraction (XRD) measurements on the calcined catalysts were performed on a Siemens D5000 instrument with Cu-Kα radiation ($2\theta = 10$ - 90°, step size = 0.02°) equipped with a Ni filter. An independent measurement of the crystallite diameters of Co_3O_4 and Ni metallic and NiO were carried out by using the Scherrer equation and assuming spherical crystallites. The Co crystallite size was estimated from that of Co_3O_4 using the following formula [3]:

$$d(Co^0) = 0.75 \cdot d(Co_3O_4)$$

according to the relative molar volumes of metallic cobalt and Co_3O_4.

Methanation

Carbon deposition studies: Temperature-Programmed Hydrogenation

Temperature-programmed hydrogenation (TPH) was used to determine the species and amount of carbon present in the methanation synthesis. Once the reaction was stopped, a He flow was run through the reactor, the reactor was cooled down to ambient temperature and driven to atmospheric pressure. Then, the outlet of the reactor was attached to a mass spectrometer and a flow of pure H_2 was run through the reactor. The hydrogen space velocity used for the hydrogenation of carbon present on the nickel surface was 233 Nml/(min•g). During the hydrogenation the temperature was linearly raised form ambient to 963 K with a ramp of 5 K/min.

A mass spectrometer monitored the signals for hydrogen, water and methane during the TPH.

Catalyst characterization

Fischer-Tropsch

Table 1 shows the physical properties of the pure support of the Co catalyst, a narrow pore γ-Al_2O_3 (10 nm), and of the Co and WGS catalysts. The typical decrease in surface area, pore volume and pore diameter of the pure support upon impregnation is seen.

Table 2 shows the physicochemical properties of the Co catalyst. The DOR after activation is similar for the ex-situ reduced and passivated sample to the in-situ reduced sample, and hence the Co particle-size estimation for the ex-situ reduced sample is similar to that for the in situ reduced sample.

The TPR profiles of the Co catalyst before and after the reduction and passivation treatments are shown in Fig. 1. The calcined catalyst (Fig. 1a) shows three peaks: peak I at 540 K has been attributed to removal of residual nitrates from the catalyst preparation [3]. Increasing the temperature, a two-step reduction of cobalt oxides [8] can be observed: peak II at 625 K is ascribed to reduction of Co_3O_4 to CoO, while the broad peak III at around 895 K corresponds to the reduction of differently sized CoO crystallites into Co.

The TPR profile of the reduced and passivated sample (Fig. 1b) shows a sharp peak at around 539 K which could probably be ascribed to the reduction of the protective outer oxide layer (CoO) formed during passivation, and a much smaller peak III, which most probably is attributable to hard-to-reduce cobalt-alumina species that were not reduced under the preceding reduction at 623 K.

Table 1.A Textural properties of support and catalysts (calcined) as determined by N_2 adsorption.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter[a] (nm)
γ-Al_2O_3	193	0.50	10.4
12Co/γ-Al_2O_3	173	0.40	9.2
30Cu/30ZnO/Al_2O_3	75	0.12	6.4

[a] The average pore diameter (dp) estimated from surface area (A) and pore volume (V) according to:
$d_p = 4V/A$

Table 2.A Physicochemical properties of the Co catalyst.

Sample	***DOR*** **(%)**	**Metal dispersion**				
		XRD		**H_2-chemisorption**		
		***d*(Co_3O_4) (nm)**	***d*(Co^0)[c] (nm)**	***D*[d] (%)**	**D_{corr}[e] (%)**	**$d(Co^0)_H$[f] (nm)**
12Co/γ-Al_2O_3	64[a]	16.8	13	5.5	8.6	11.2
12Co/γ-Al_2O_3 red+pass	62[b]	-	-	-	-	-

[a] Estimated by H_2-TPR after reduction at 623 K for 16 h in H_2.
[b] Estimated by H_2-TPR after activation at 493 K for 2 h in H_2.
[c] Cobalt particle size according to Eq. (2).
[d] Metal dispersion, after reduction at 623 K for 16 h in H_2.
[e] Dispersion corrected for *DOR*.
[f] Cobalt particle size according to Eq. (1).

Methanation

The BET surface areas calculated are 18 m^2/g and 143 m^2/g for TiO_2 and Al_2O_3 supports, respectively.

The particle size was determined by XRD on the catalysts in their nickel oxide and nickel metallic states. The results are presented in Table 1.

Table 3.A: Particle size before and after reduction of the catalysts determined by XRD

Catalyst	**Before reduction (nm)**	**After reduction (nm)**
20%Ni/Al_2O_3	-	9
20%Ni/TiO_2	24	24

Due to the size of the molecules of NiO and $Ni^{(0),}$ the crystal diameter should decrease after reduction. However, the nickel diameter was the same as the nickel oxide diameter when supported on titania. A possible explanation for this particle growth is that the particles sintered during the reduction at 773 K.

Observing these TPR results, it can be assumed that the DOR of the reduction treatment used for the titania-supported catalysts (4h at 773 K with pure hydrogen) would be close to 100%. Therefore, another TPR after the reduction treatment to calculate the DoR was not performed. However, this evaluation was performed on the alumina-supported catalyst. The calculated DOR reduction of 20%Ni/Al_2O_3 was 96%.

The hydrogen chemisorption data obtained from the analysis of the previously reduced titania-supported nickel catalyst turned out to be incoherent due to the fact that the physisorbed quantity was almost the same as the physisorbed and chemisorbed quantities together. It is stated in [9], that the H_2 adsorption properties are changed with the presence of TiO_x species formed during the reduction and that the H_2 adsorption capacity decreases if TiOx is present on the nickel surface. Therefore, H_2 chemisorption is probably not an accurate method for calculating dispersion on titania-supported catalysts. In contrast, the alumina-supported catalyst could be analyzed with H_2 chemisorption. The dispersion obtained was 9%.

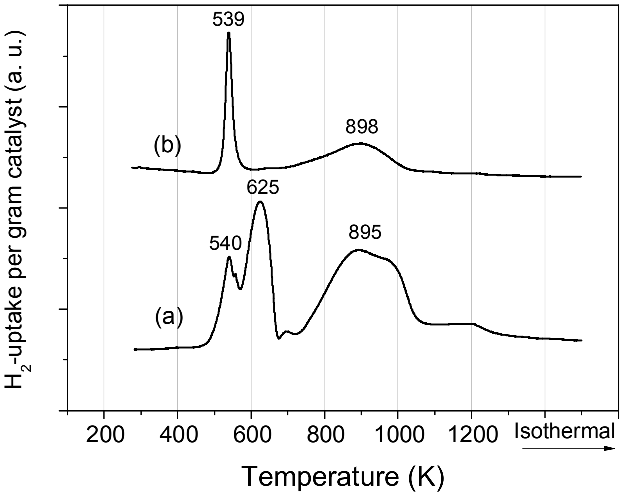

Figure 1.A H_2-TPR profile for calcined Co catalyst (a) and reduced and passivated Co catalyst (b).