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# Improvement of Pt-based catalyst supported on CeZrO<sub>2</sub> used for the high-temperature water-gas shift reaction

by

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## Abstract

The iron-chromium (Fe/Cr) catalyst is used for high-temperature water-gas shift (HT WGS) reaction. A major concern using the Fe/Cr catalyst is that it contains hexavalent chromium ( $\text{Cr}^{+6}$ ) which is a potent carcinogen causing health and environmental issues. In order to reduce the usage of chromium in industrial HT WGS applications, a chromium-free catalyst needs to be developed.

The aim of this thesis project was to develop a chromium-free catalyst which shows high activity, selectivity, and stability during HT WGS operating conditions. Six different formulations, catalysts A-F, were prepared for the experimental part of the project. The prepared catalysts were then compared to the activity and selectivity performance of a commercial Fe/Cr catalyst.

The tests were performed in a reactor containing 3 ml of the catalyst and 3 ml of inert material (alfa-alumina). The particle size of the catalysts and the inert material was 1-2 mm. Feed containing 10.8 % CO, 29.8 %  $\text{H}_2\text{O}$ , 43.2 %  $\text{H}_2$  and 16.2 %  $\text{CO}_2$  was mixed and introduced to the reactor (Gas hourly space velocity:  $20,000 \text{ h}^{-1}$ ). The outlet dry gas was analysed by gas chromatography at temperatures 350 °C, 400 °C, 450 °C and 500 °C. The system was operating at atmospheric pressure.

The short-term activity and selectivity tests show that the catalysts E exhibits CO conversion up to 72 % at 350 °C (the maximum CO conversion is 79.3 % at 350 °C due to equilibrium). Compared to the commercial Fe/Cr catalyst, which exhibits 37.8 % at 350 °C, the activity of the catalyst E is significantly higher. None or very low concentrations of hydrocarbons were produced, implying that the catalyst is selective towards the desired products,  $\text{H}_2$  and  $\text{CO}_2$ . The other prepared catalysts, Pt/Re/CeZrO<sub>2</sub> and Pt/Re/TiO<sub>2</sub>, performed poorly in terms of selectivity. Pt/Re/CeZrO<sub>2</sub> produced as much as 5.97 % methane at 450 °C. The Pt/Re/TiO<sub>2</sub> catalyst produced 0.16 % methane at 450 °C. Because of the methane formation, it was concluded that the Pt/Re/CeZrO<sub>2</sub> and Pt/Re/TiO<sub>2</sub> catalyst formulations are not suitable for HT WGS applications, and were therefore not further studied in the long-term stability test.

The long-term stability tests were performed on the catalyst E. No deactivation signs were noted during the 135 hours on-stream and reactor temperature at 400 °C.

The thesis project presents successful results from the experiments performed on the developed chromium-free catalyst for HT WGS applications. In terms of the activity and selectivity, it is concluded that catalyst E exceeds the performance of a commercial Fe/Cr catalyst. Stability results show that the catalyst is stable for at least 135 hours, not indicating any deactivation signs.

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## 1. Introduction

The global demand for pure hydrogen is increasing rapidly and has grown more than threefold since 1975. [1] Oil refineries, ammonia plants and methanol synthesis plants are the largest hydrogen consuming industries, demanding more than 90 % of the produced hydrogen every year. [2] Industrial production of hydrogen is generally performed through steam methane reforming (SMR) followed by the water-gas shift reaction (WGS). The WGS is essential to produce pure hydrogen and is considered as one of the most important industrial processes. In the reaction, carbon monoxide (CO) and steam (H<sub>2</sub>O) is converted to carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>).

In typical industrial applications, WGS is conducted as two-stage process. The first stage, high-temperature WGS, is operated at temperatures 310 – 450 °C and pressures 10 to 60 bar. The inlet gas can consist of as much as 50 % CO (on a dry basis) which is reduced to 3 – 4 % in the outlet gas. The second stage, low-temperature WGS, is performed at 150 – 250 °C, reducing CO content to 0.5 %. [3]

Commercially, iron-chromium (Fe/Cr) based catalyst is used for high-temperature WGS reaction. However, a major issue with this catalyst is that it contains hexavalent chromium (Cr<sup>6+</sup>), which is a potent carcinogen causing long-term harm for humans, other organisms and the environment. To reduce the use of chromium in high-temperature water-gas shift applications, many researchers have shifted their work towards developing a chromium-free catalyst. However, in terms of overall activity and cost, Fe/Cr catalyst is up to this day the most efficient catalyst used in large-scale HT WGS applications. [2] Thus, more research is needed in order to replace the Fe/Cr catalyst with a chromium-free one, which is what this thesis project intends to do.

### 1.1. Aim of work

There is a vast interest among the industries to develop a chromium-free catalyst for high-temperature water-gas shift applications. Two major factors determine whether the new catalyst formulation is suitable for the industrial applications or not; (1) the catalytic activity, selectivity and stability must show equivalent or exceed the performance of a commercial Fe/Cr catalyst and, (2) the price of the catalyst should be competitive compared to the price of a commercial Fe/Cr catalyst.

The aim of this work is to develop a catalyst that can be applied in HT WGS applications, and which does not contain any chromium. The work will be performed by (1) researching studies performed on chromium-free catalysts, (2) by composing new formulations based on information found in the literature and, (3) by measuring the activity, selectivity, and stability of the new catalyst formulations during HT WGS operating conditions. The Pt/Re supported

on CeZrO<sub>2</sub> catalyst is chosen to be the starting-point catalyst for the work. Three following questions are aimed to be answered in this thesis project:

- (1) Is a Pt/Re catalyst supported on CeZrO<sub>2</sub> suitable for HT WGS applications?
- (2) Does changing the support of Pt/Re/CeZrO<sub>2</sub> increase the activity, selectivity, and stability of the catalyst?
- (3) Does changing the promoter of Pt/Re/CeZrO<sub>2</sub> improve the activity, selectivity, and stability of the catalyst?

The catalytic performance of the new catalyst formulations will be compared with the catalytic performance of a commercial Fe/Cr catalyst in the experimental part.

## 1.2. Report structure

The outline of this thesis study constitutes five sections. In the introduction section, the research questions for this thesis project are formulated. In the second part, an introduction to the heterogeneous catalysis and the water-gas shift reaction is done, and recent advances in chromium-free catalysts are presented. The third section presents the experimental procedure, which includes catalyst formulation, system design set-up and test plan for the performed experiments. Also, analytical instruments used in order to analyse the catalyst activity and stability are presented. The fourth section contains results from the performed catalysts and are discussed. The fifth and last section concludes and answers the research questions of this master thesis and provides further research suggestions in order to improve and develop the chromium-free catalysts.

## 2. Background

The following section describes heterogenous catalysis, the water-gas shift reaction (WGS) and the commercial catalysts used for this application. Furthermore, recent advances about chromium-free catalysts and deactivation mechanisms are presented.

### 2.1. Heterogeneous catalysis

Heterogeneous catalysis is a common industrial process where reactants, typically in the gas or liquid phase, are introduced to solid material (catalyst), which has the main task to activate the reaction. The composition and structure of a catalyst vary, but generally, they do consist of (1) a carrier, (2) a support, and (3) an active phase. [4]

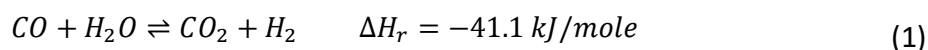
The carrier gives structure to the catalyst and can be described as a skeleton giving the active phase a surface to attach itself to. The surface area of the carrier is an important factor in the catalyst formulation since it determines the diffusion of the reactant/product, heat-transfer properties and pressure drop of a chemical reactor. A support can be added to the carrier to increase the surface area further and is often applied in catalysts to improve the aforementioned properties. [4]

The active phase has the property of activating the reactants. The interaction of reactants takes place on the sites of the active phase. Therefore, it is important that the active phase is dispersed over the carrier evenly. The active phase can consist of non-precious metals such as Fe, Zn and Cu or noble metals such as Pt, Au, Pd, Rh and Ag. [4]

Aside from the carrier, the support and the active phase, promoters or modifiers can be added to a catalyst. The addition of a promoter or a mixture of promoters can increase the activity, selectivity towards desired products and stability of the catalyst. [4]

### 2.2. Water-gas shift reaction

Water-gas shift reaction is a reversible and moderately exothermic reaction (1) where carbon monoxide (CO) and steam (H<sub>2</sub>O) is converted to hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>), as shown below. [5]



The reaction is ruled by equilibrium, and CO conversion is favoured at low reaction temperatures. However, at low temperatures, the reaction is limited by kinetics, and higher temperatures are required in order to increase the reaction rate. The pressure does not influence the equilibrium due to the reaction being equimolar, although it increases the reaction rate up to equilibrium when applied in the process. [6] In figure 1, the equilibrium

constant is presented for the WGS reaction. The equilibrium constant decreases with increased temperature.

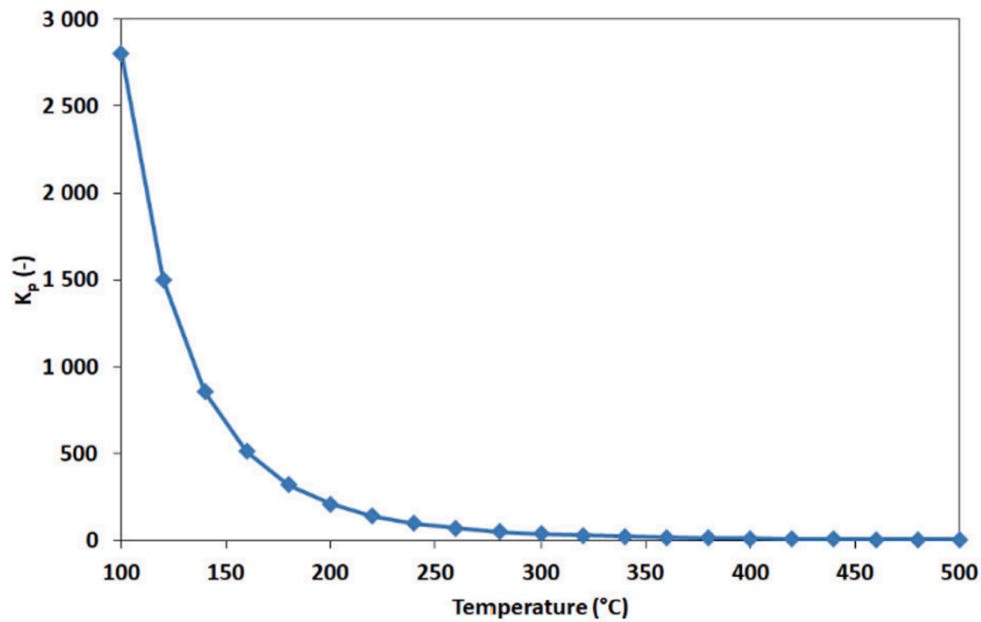


Figure 1. The equilibrium constant ( $K_p$ ) as a function of temperature.[2]

In addition to the temperature, the equilibrium is also affected by the feed composition. The equilibrium can be shifted towards the products  $H_2$  and  $CO_2$  if more steam is added to the feed and the steam/CO ratio is increased. Figure 2 shows how different steam-to-CO ratios (R) affect the equilibrium. [5] As seen in the figure, the steam-to-CO ratio becomes more important with increased temperatures.



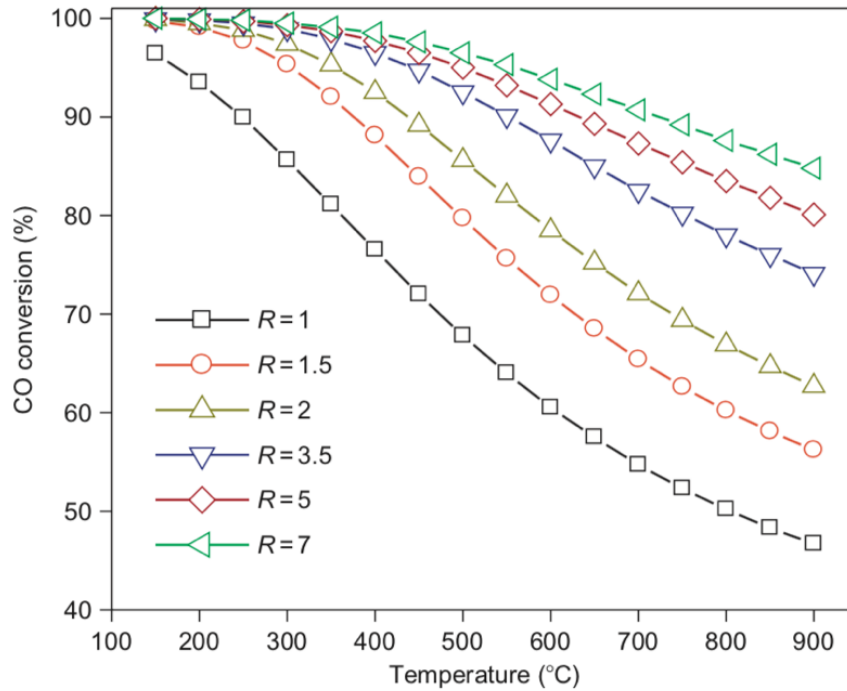


Figure 2. The steam-to-CO ratio ( $R$ ) effect on the equilibrium. [5]

In industrial applications, the water-gas shift reaction is conducted as a two-stage process. Firstly, a high-temperature water-gas shift (HT WGS) step and secondly, a low-temperature water-gas shift (LT WGS) step. Usually, two adiabatic fixed bed reactors are used with an intermediate cooling step. This thesis project is limited to focusing on the high-temperature WGS process.

### 2.2.1. High-temperature water-gas shift

Industrially, the high-temperature WGS reaction is operated at temperatures of 310 – 450 °C and with the total pressure varying between 10 and 60 bar. The space velocities are kept below 20,000 h<sup>-1</sup>. Typical feed compositions entering the HT WGS reactor are presented in the table 1. [7]

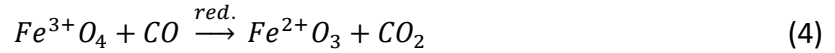
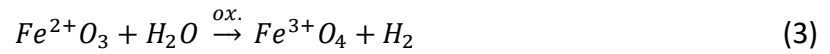
Table 1. The typical dry exit gas composition from steam reforming for hydrogen production.[7]

Compound	Vol.%
CO	0.128
CO <sub>2</sub>	0.080
H <sub>2</sub>	0.578
CH <sub>4</sub>	0.004
N <sub>2</sub>	0.211

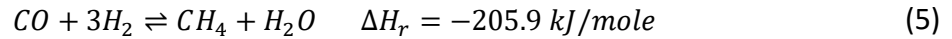
### 2.3. Commercial catalysts for high-temperature WGS

The iron-chromium (Fe/Cr) based catalyst was discovered in 1914 by Bosch and Wild from BASF. It has since then been the most used catalyst for the high-temperature WGS reaction in industrial applications. [2] The composition of the catalyst is generally 80 – 90 wt.% hematite ( $\text{Fe}_2\text{O}_3$ ) and 8 – 10 wt.% chromium oxide ( $\text{Cr}_2\text{O}_3$ ), the rest being promoters and stabilizers such as  $\text{CuO}_2$ ,  $\text{Al}_2\text{O}_3$ , alkali,  $\text{MgO}$  and  $\text{ZnO}$ . [3]

The active phase of the catalyst is magnetite ( $\text{Fe}_3\text{O}_4$ ) which is formed by partial reduction of hematite ( $\text{Fe}_2\text{O}_3$ ), and the activity is linked to  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple where  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  by  $\text{H}_2\text{O}$  and  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  by  $\text{CO}$  as shown in reaction 3 and 4. [8]



Chromium oxide is added to the catalyst since magnetite is sensitive to thermal sintering and over-reduction during WGS operation conditions. The addition of chromium stabilizes the catalyst and decreases the sintering of the active phase. Furthermore, the added chromium prevents over-reduction of magnetite to  $\text{FeO}$ , metallic iron and iron carbides. Over-reduction is un-desirable as the metallic iron and iron carbides catalyze methane production through reaction (5). [8]



A major concern about the iron-chromium based catalyst is the presence of hexavalent chromium ( $\text{Cr}^{6+}$ ) which is a potent carcinogen causing health and environmental issues. Hexavalent chromium is present on the surface of the fresh catalyst and is subsequently reduced to  $\text{Cr}^{3+}$  during HT WGS conditions. In, USA, strict guidelines have been implemented in order to reduce exposure of hexavalent chromium and in Europe, hexavalent chromium has already been banned in electrical equipment. [9] Despite the major harm risk caused by the hexavalent chromium, Fe/Cr still remains the market-leading catalyst for HT WGS applications due to its catalytic performance and the low cost. [2]

However, a recently developed chromium-free catalyst is challenging the commercial Fe/Cr catalyst on the market. This catalyst, developed and patented by Haldor Topsoe in 2012, can be purchased and used in commercial HT WGS applications. [10] According to the patent, the catalyst consists of zinc oxide spinel and zinc oxide, and is combined with alumina. Furthermore, it is promoted with an alkali metal (Na, K, Rb, Cs or a combination of those). [11] Studies performed on this catalyst show that it exhibits superior activity and thermal stability compared to the Fe/Cr catalyst. [12]

## 2.4. Recent advances in chromium-free catalysts for HT WGS

In this section, studies on recent advances in chromium-free catalysts are presented. The section describes the iron-based and the noble metal-based catalysts.

### 2.4.1. Chromium-free iron-based catalysts

Many attempts have been made to modify the commercial iron-chromium catalyst by replacing chromium with other dopants. For instance, the addition of Al and Al/Cu instead of chromium have been reported as promising by Araujo and Rangel. [13] The researchers found that Cu alone does favour sintering of Fe-based catalysts, but this can be prevented by the addition of Al. Adding Al to iron oxide increases the surface area significantly, which is important for HT WGS catalysts. It is claimed that the combination of Al and Cu does more easily produce the active phase (magnetite) compared to other catalysts in the study. It is also resistant to further reduction of magnetite and shows a similar activity as the commercial Fe/Cr catalyst. Reddy *et al.* investigated how co-doping Fe/M (M = Cr, Ce, Ni, Co, Mn and Zn) with Cu affected the catalyst activity. [14] It was found that adding Cu increased the conversion of CO in all catalysts except for Fe/Ce. A decrease in activity for Cu-doped Fe/Ce catalysts were also observed in other studies. [15]

Another metal that has been studied as a replacement for chromium is nickel. The promotion of nickel has shown high CO conversion and is a promising substitute for chromium in Fe-based HT WGS catalysts. Nickel does, however, catalyse methanation and needs to be modified in order to suppress methane formation. Meshkani and Rezaei performed experiments where alkali promoters (Na, K, Cs and Li) were added to Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-NiO catalyst in order to investigate the CO conversion and methanation activity. [16] The addition of these promoters resulted in decreased methane formation. It was concluded that catalyst promoted with 3 wt.% Na showed the highest catalytic activity and the lowest methane formation in the performed experiments. In further work, Meshkani and Rezaei studied the addition of Ba to Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-NiO catalyst and concluded that methane formation could be significantly suppressed when Ba was used as a promoter. [17] The CO conversion rate and stability of the catalysts showed great performance, where the addition of 3 wt.% Ba resulted in the best HT WGS activity. [18] Another study performed by Fuentes *et al.* showed that adding Zn in Ni-based catalyst also suppresses methanation. [19] However, the reported study was performed in a temperature range of 200 – 350 °C and did therefore not completely represent HT WGS conditions.

### 2.4.2. Noble metal catalysts

Noble metals such as platinum (Pt), gold (Au), rhenium (Re), rhodium (Rh) and palladium (Pd) are highly active for WGS reaction. Pt, Rh and Pd are thoroughly studied noble metals for HT WGS catalysts. It has been shown that when using noble metals, it is important that they are supported on partially reduced oxides such as cerium oxide (CeO<sub>2</sub>), zirconium oxide

(ZrO<sub>2</sub>), titanium oxide (TiO<sub>2</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and mixed oxides. [2] The reason is that these catalysts are bifunctional, meaning that both the active metal as well as the support participate in the WGS reaction. This is due to the strong metal-support interactions where the metal sites activate carbon monoxide, and the support activates the water. [3] Moreover, the active phase and carrier participation in the reaction has also been proved by performing tests on noble metals on non-reducible supports such as SiO<sub>2</sub>. For instance, Rh/CeO<sub>2</sub> (reducible support) have shown that the catalyst is active while Rh/SiO<sub>2</sub> (irreducible support) catalyst is not, proving that both the active metal and the support is important and do participate in WGS reaction. [20]

#### 2.4.2.1. Active phase

When using the noble metals previously mentioned, Pt, Pd or Rh, the catalyst can be coated with either one or a combination of these metals. A monometallic catalyst is coated with only one noble metal, bimetallic with two different noble metals and polymetallic with a combination of three or more.

Pt-based catalysts supported on CeO<sub>2</sub> are very active for HT WGS reaction and has been reported as the most prominent formulation for WGS reaction. [21] However, a major drawback of Pt-based catalysts supported on CeO<sub>2</sub> is methane formation which tends to appear at temperatures above 375 – 425 °C. At higher temperatures, 425 – 450 °C, Pt also shows sintering effects and limits the long-term stability. Methanation tendencies also appear on Rh and Pd when supported on partially reduced oxides. However, when comparing methane selectivity of the noble metal catalysts, it has been reported that among the noble metals Pt, Pd, Ru and Rh, Pt/CeO<sub>2</sub> and Pd/CeO<sub>2</sub> are the ones showing the lowest methane formation. [22] Ru followed by Rh show the highest methane formation.

In a comparative study, Thion *et al.* prepared 21 different catalysts based on noble metals Pt, Au, Cu, Rh, Pd and Ru which were supported on either CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>. The aim of the study was to compare the activity and selectivity of a large number of catalysts during identical operating conditions. The temperatures investigated were 250 °C, 300 °C and 350 °C with a feed composition of 10 % CO, 10 % CO<sub>2</sub>, 20 % H<sub>2</sub>O, 30 % H<sub>2</sub> and 30 % Ar. The most active formulations in the study were Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub> catalysts, while Rh- and Ru- based catalysts showed significantly higher methane formations. [23]

Zhao and Gorte studied noble metals Pd, Pt and Rh on CeO<sub>2</sub> and CeO<sub>2</sub>/ZrO<sub>2</sub> support doped with iron oxide. [24] In the study, they found that adding iron to Pd/CeO<sub>2</sub> catalyst increases the reaction rate of WGS significantly, while no change in reaction rate was noted when iron oxide was added to Pt/CeO<sub>2</sub> or Rh/CeO<sub>2</sub>. It was proposed that the activity is favoured by the Fe-Pd alloy formation, which is driving the reduction of hematite to magnetite (the active phase). Iron oxide catalysts supported on ceria were also studied by Bali *et al.* [25] The catalysts were doped with 1 wt.% and 2 wt.% Pd and the results of the performed study

showed that addition of 1 wt.% Pd to Fe/Ce performed approximately 5 times better compared to Pd/Ce catalyst. Undoped Fe/Ce catalyst showed no activity at all.

#### 2.4.2.2. Partially reduced supports

The support of noble metal-based catalysts plays a crucial role in the activity and stability performance. [26] CeO<sub>2</sub> is excellent support for noble metal catalysts due to its oxygen storage capacity. During oxidizing reaction conditions, the oxygen is stored in the lattice of CeO<sub>2</sub>, and during reducing conditions, the oxygen is released. It has been found that CeO<sub>2</sub>-based mixed metal oxides show even better activity performance compared to pure CeO<sub>2</sub>. For instance, the addition of rare-earth elements such as Zr<sup>4+</sup> or La<sup>3+</sup> facilitates reduction/oxidation behavior due to modifications of the lattice. Thermal stability can also be improved by adding rare-earth elements and/or zirconium due to the ability to inhibit crystal growth. [20] Palma *et al.* compared the activity performance of Pt supported on CeO<sub>2</sub>, CeO<sub>2</sub>/ZrO<sub>2</sub> and CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. It was proved that Pt on the mixed oxide CeO<sub>2</sub>/ZrO<sub>2</sub> showed the best activity and selectivity performance. [27]

Azzam *et al.* compared the activity of Pt-based catalysts supported on TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub> and mixed combinations of the supports. Among the catalysts studied, Pt/TiO<sub>2</sub> achieved the highest activity and stability. It was further investigated how the addition of Re or Sn affected the activity and stability of the catalyst. The results indicated that the addition of Re significantly increased the WGS reaction rate, while the addition of Sn demonstrated very low activity compared to undoped Pt/TiO<sub>2</sub>. [28] It must, however, be noted that both of the aforementioned studies were performed with gas feed consisting of only CO, H<sub>2</sub>O and inert gas, which does not represent the industrial feed composition.

#### 2.4.2.3. Promoters

There are several purposes for adding a promoter to HT WGS catalyst. The major purposes found in the literature are; (1) to increase the activity of the catalyst, (2) to suppress methane formation and (3) to suppress deactivation, for instance, thermal sintering and/or over-reduction. [4]

Re is a well-known promoter increasing the activity of noble metal-based HT WGS catalysts.[29] In a study, Azzam *et al.* compared the activity of Pt/TiO<sub>2</sub>, Re/TiO<sub>2</sub> and Pt-Re/TiO<sub>2</sub> catalysts with the aim to understand the role of Re in Pt-Re/TiO<sub>2</sub> catalysts. The researchers claimed that the reason for the enhanced activity in the presence of ReO<sub>x</sub> species during the WGS reaction conditions. Simply put, ReO<sub>x</sub> provides another redox route for the reactants to yield CO<sub>2</sub> and H<sub>2</sub>, increasing the catalytic activity. In another study, Choung *et al.* prepared several Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts promoted with Re, La or Rh in order to compare the activity of promoted and un-promoted catalysts. [30] Re promoted catalyst showed superior performance, both when it comes to the activity and hydrogen selectivity. Promotion with La or Rh performed worse than un-promoted Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst. Promotion with Rh also tended to catalyze methanation at temperatures above 270 °C.

In order to suppress methane formation, Korotkith *et al.* proposed and patented a Pt/CeO<sub>2</sub>-ZnO catalyst. [20] The inventors claimed that the addition of basic metal oxides such as MgO, CaO, SrO, BaO or ZnO reduces methane production, whereas the addition of ZnO showed the best methane suppression performance.

## 2.5. Catalyst deactivation

Loss of catalytic activity or selectivity over time is a common and concerning problem during catalytic processes. Industrially used Fe/Cr-based catalysts are in operation for 3 – 5 years before being replaced with new, fresh catalyst. [3] However, the stability of chromium-free catalysts has been reported as poor compared to the Fe/Cr catalyst. By modification of the formula with the right carriers and promoters, the life length of chromium-free catalysts can be significantly improved. [31] Therefore, when creating new formulations, it is of great importance to understand the mechanisms of catalyst deactivation. Different theories for the catalyst deactivation during WGS operation conditions have been presented in the literature:

- Thermal sintering of the noble metal/support
- Over-reduction of the active phase/support
- Fouling and H<sub>2</sub>S poisoning

Initial deactivation of the catalyst does always occur during the start-up of the process. The catalyst does usually become stable after being brought on-stream for 50 – 100 hours. Beyond that, the catalyst life length is determined by the operating conditions and the process hygiene.[4]

### 2.5.1. Thermal sintering

Thermal sintering is a common deactivation mechanism that results from either (1) catalytic surface area being reduced due to crystalline growth of the active phase or (2) the support area being reduced due to support collapse. Crystalline growth can occur either by atomic migration or crystallite migration, as presented in figure 3. Atomic migration is when single metal atoms are detached and migrated over the support until being captured by larger crystallites. Crystallite migration is when the entire crystallite is migrating over support, colliding with another large crystallite. Thermal sintering is an irreversible deactivation mechanism and results in decreased activity due to less available active phase sites for the reactant compounds to attach. [31]

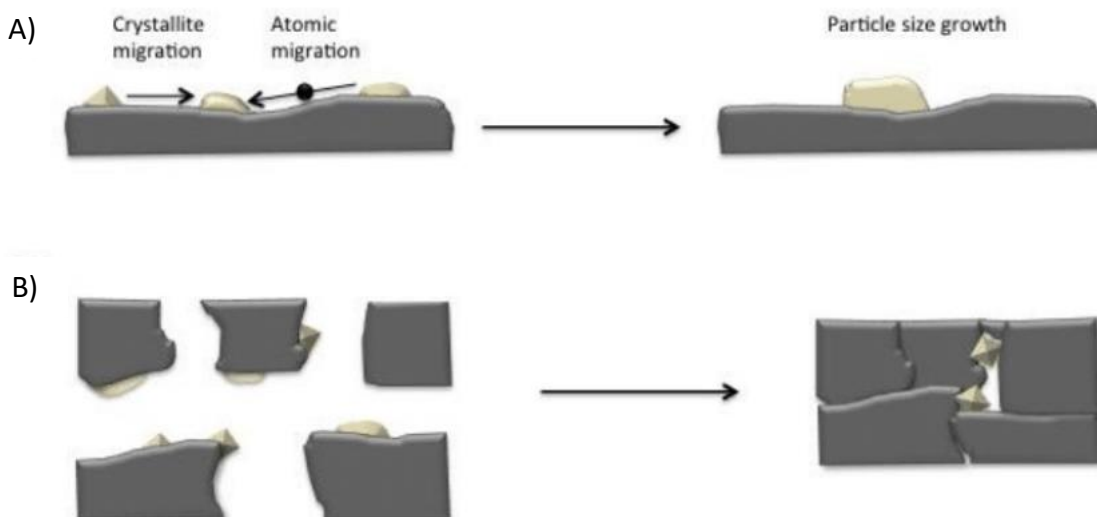


Figure 3. The deactivation mechanism illustrated. (A) Sintering by crystallite migration and atomic migration, and (B) sintering of the support. Reproduced with permission. [4]

Thermal sintering of a catalyst is unavoidable, and some sintering will occur during start-up and normal operating conditions. For the commercial Fe/Cr catalysts, approximately 50 % of the total surface area is reduced during the first months of the operation. Further, 25 % is lost during the remaining life of the catalyst. [2]

#### 2.5.2. Over-reduction of the active phase/support

Irreversible and reversible over-reduction of either the active phase or the support have been reported by studies. It is well-known that iron is sensitive to over-reduction and that in the cases where magnetite is reduced to metallic iron and iron carbides, it leads to methanation.[8]

Irreversible over-reduction has been reported on partially reduced oxide supports. In a performed study, Zalc *et al.* investigated how the deactivation rate of the Pt/CeO<sub>2</sub> catalyst was affected when introducing high fractions of hydrogen to the feed. The researchers found that the deactivation rate increased significantly in the presence of hydrogen. It is thought that the hydrogen creates an environment that facilitates the irreversible over-reduction of the support and that this deactivation mechanism is universal for all noble metal/ceria-based catalysts. Therefore, during the real-life WGS operating conditions, the irreversible over-reduction will occur for these types of catalysts according to the authors. [32]

#### 2.5.3. Fouling and H<sub>2</sub>S poisoning

Fouling is a deactivation mechanism where the compounds, either reactants, products or feed impurities, are covering the active phase or plugging the pores. The covering prevents the reactants to reach the active phase, resulting in catalyst deactivation. Figure 4 illustrates fouling and poisoning deactivation mechanisms. [4]



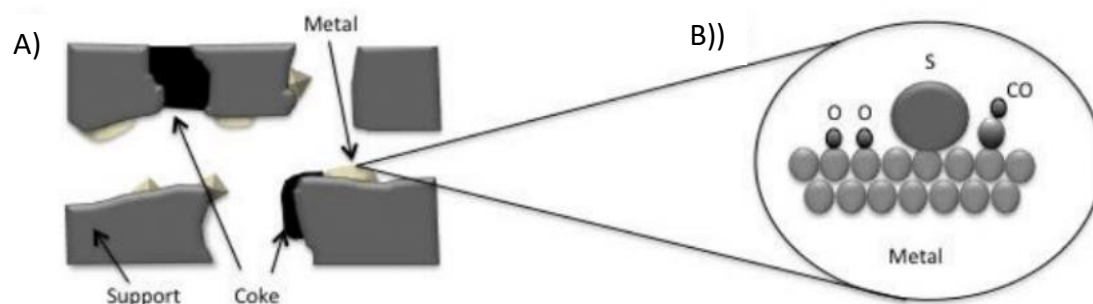


Figure 4. The deactivation mechanisms through (A) fouling and (B) poisoning. Reproduced with permission. [4]

Poisoning is a common deactivation mechanism occurring due to strong chemisorption of the reactants, products and/or impurities on the active sites of the catalyst. For instance, nickel-based catalysts are very sensitive to sulphur ( $\text{H}_2\text{S}$ ) since the poison strongly adsorbs on nickel-metal surfaces. Generally, the poisoning of nickel-metal surfaces is rapid and irreversible. However, it can be prevented by adding promoters such as Mo and B, which selectively adsorb sulphur. [31]

Studies have reported that noble metal-based catalysts exhibit very poor performance in the presence of  $\text{H}_2\text{S}$ . [33] Xue *et al.* reported that the activity of Pt/ZrO<sub>2</sub> catalyst decreases with increased concentrations of sulphur. In the study, the reported conversion decreased from 44 % (0 ppm  $\text{H}_2\text{S}$  in the feed) to 25 % (50 ppm  $\text{H}_2\text{S}$  in the feed) to 14 % (200 ppm  $\text{H}_2\text{S}$  in the feed). Once the sulphur was removed from the feed, the conversion returned to 44%. [34]

## 2.6. Price of the raw material for catalyst preparation

Besides the catalytic activity, selectivity and stability performance, the price of the catalyst is another important factor for the industries. The price per kg for the non-precious metals and noble metals are presented in table 2. As presented, the price of the noble metals is significantly higher. Therefore, for a noble metal catalyst to be competitive on the market against the Fe/Cr catalyst, the costs have to be comparative or the life time and the performance has to be superior. However, the economic analysis of a catalyst formulation is not in the scope of this thesis work and the presented table is only included for the completeness of the work.

Table 2. Noble metal price [\$/g]. The prices are noted on 11/1-2021.

Non-precious metals	Price [\$/kg]	Noble metals	Price [\$/kg]
Cu	9.7588	Pt	31232.20
Fe	0.1245	Pd	61523.35
Al	2.96	Rh	562638.06



<b>Ni</b>	20.929	<b>Ru</b>	17682.91
<b>Zn</b>	3.6070		

## 2.7. Conclusions of the literature survey

Based on the information and the results from the studies presented, the important properties for HT WGS catalysts are:

- High activity during HT WGS operating conditions (310 – 450 °C)
- No methane formation or Fisher-Tropsch products during the HT WGS operating conditions
- High thermal stability without deactivation for at least 3 – 5 years

Comparing the results from the different studies is difficult due to variations in preparation methods of the catalysts and different experiment operating conditions. In many cases, the catalysts have been tested with a feed mixture of only water and carbon monoxide. However, the reaction products hydrogen and carbon dioxide are known to have an inhibiting impact on the reaction rate. [23] Also, the introduction of H<sub>2</sub> to the feed enhances the methane formation and/or over-reduction during HT WGS operating conditions. Other factors affecting catalytic performance can be catalyst particle size, reactor et cetera.

It is, however, concluded that when it comes to precious metal catalysts, the noble metals Pt and Pd are the most suitable for HT WGS. To achieve high activity with Pt and/or Pd, these metals should be supported on partially reduced oxides such as CeZrO<sub>2</sub> and/or TiO<sub>2</sub>. Furthermore, a promotion with Re increases the catalytic activity.

To enhance the selectivity, the literature suggests promotion of the catalyst with either an alkali metal such as Na or basic metal oxides such as MgO or ZnO. In figure 5, the recipe for a chromium-free catalyst formulation is concluded and presented.

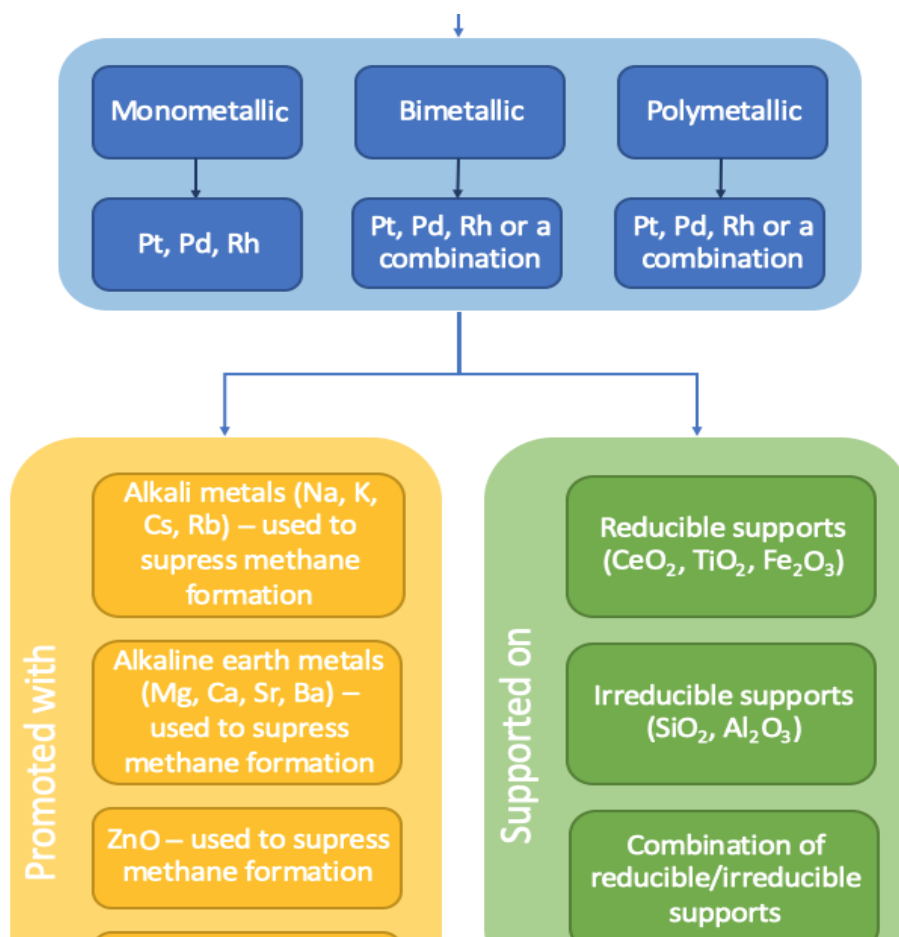


Figure 5. The conclusion of the literature survey for the preparation of catalyst formulations using noble metal.

### 3. Experimental procedure

This section describes catalyst preparation and system design for the experimental part of the thesis project.

#### 3.1. Catalyst preparation

For the experimental part, six catalyst formulations were prepared. The formulations are presented in table 3. Iron-chromium catalyst used as a reference catalyst was purchased from AlfaAesar.

Table 3. Reference catalyst and new formulations were prepared for the experimental part in this thesis project.

	<b>Support</b>	<b>Promoter/Modifier</b>	<b>Active phase</b>
<b>Catalyst Ref.</b>	-	7% Cr(III)oxide, 5% CuO	82.7% Fe <sub>2</sub> O <sub>3</sub>
<b>Catalyst A</b>	Ce <sub>0.53</sub> Zr <sub>0.47</sub> O <sub>2</sub>	0.2% Re	3% Pt
<b>Catalyst B</b>	Ce <sub>0.53</sub> Zr <sub>0.47</sub> O <sub>2</sub>	0.2% Re	1.5% Pt
<b>Catalyst C</b>	TiO <sub>2</sub>	0.2% Re	3% Pt
<b>Catalyst D</b>	TiO <sub>2</sub>	0.2% Re	1.5% Pt
<b>Catalyst E</b>	Ce <sub>0.53</sub> Zr <sub>0.47</sub> O <sub>2</sub>	X% Alkali metal	3% Pt/ Y% Transition metal
<b>Catalyst F</b>	Ce <sub>0.53</sub> Zr <sub>0.47</sub> O <sub>2</sub>	X% Alkali metal	1.5% Pt/ Y% Transition metal

##### 3.1.1. Catalysts supported on Ce<sub>0.53</sub>Zr<sub>0.47</sub>O<sub>2</sub>

Ceria-zirconia based catalysts were prepared by the incipient wetness method. The support was prepared by mixing 200 g of CeO<sub>2</sub> and ZrO<sub>2</sub> powder (Actalys 9447, Solvay) with 100 g of boehmite (AL20DW, Nyacol) and 19.5 g of distilled water in a beaker. A spoon was used to mix the ingredients until the mass looked homogeneous. It was further put in a ceramic vessel and placed in a furnace with a temperature set to 80 °C for 16 hours followed by 120 °C for 7 hours, followed by calcination at 500 °C for 4 hours. Once the furnace had cooled down, the vessel was taken out, and the solid mass was crushed in a mortar and physically sieved to particles 1 – 2 mm. Water up-take was measured on the prepared carrier, which showed a value of 0.38 g H<sub>2</sub>O/g carrier.

For catalyst A, a mixture of water, Pt(NO<sub>3</sub>)<sub>2</sub> solution, and Re was prepared. The support was coated with the mixture, resulting in Pt and Re concentrations of 3 wt.% 0.2 wt.% respectively. For catalyst B, the support was coated with 1.5 wt.% Pt and 0.2 wt.% Re. The catalysts were dried and calcined in a furnace, first using a drying step at 120 °C for 4 hours followed by the calcination step at 500 °C for 4 hours. The preparation of catalysts E and F are not revealed in this report.

### 3.1.2. Catalysts supported on TiO<sub>2</sub>

Catalysts C and D supported on TiO<sub>2</sub> were prepared by crushing and sieving TiO<sub>2</sub>-pellets (AlfaAestar) to 1 – 2 mm. The water uptake was measured and calculated to a value of 0.32 g H<sub>2</sub>O/g carrier. A mixture containing Pt(NO<sub>3</sub>)<sub>2</sub> solution, Re and water was prepared. A pipette was used to coat the TiO<sub>2</sub> support resulting in Pt concentration of 3 wt.% on catalyst C and 1.5 wt.% on catalyst D. Re-content was 0.2 wt.% for both catalysts. The catalysts were dried and calcined in a furnace, first using a drying step at 120 °C for 4 hours followed by the calcination step at 500 °C for 4 hours.

All catalysts were reduced using 8.8 % H<sub>2</sub>, the balance being N<sub>2</sub> for one hour and in 350 °C before HT WGS feed was introduced to the reactor.

### 3.2. System design

The experimental part of the thesis project was performed in a system set-up which is presented in figure 6. Gases introduced to the system were CO, CO<sub>2</sub>, H<sub>2</sub> and steam (H<sub>2</sub>O), and the flow of the gas was controlled by four different mass flow controllers (MFC).

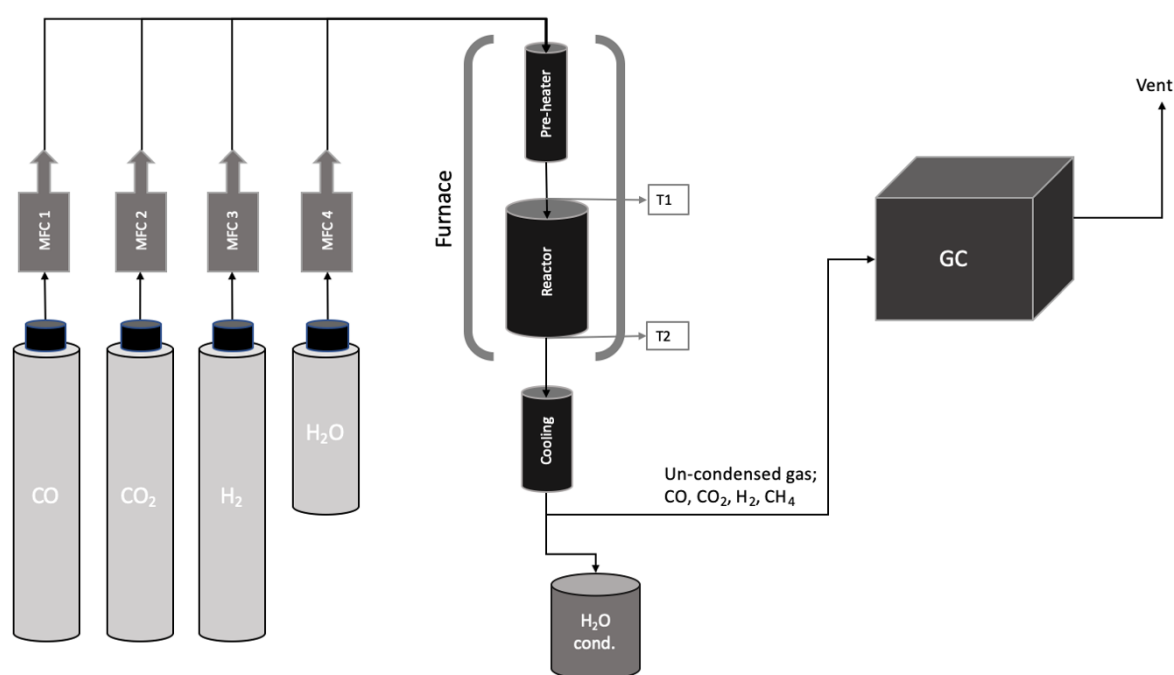


Figure 6. System set-up for the experimental part.

The inlet gas was mixed and heated in a pre-heater before entering the reactor containing 3 ml of a catalyst and 3 ml of alfa-alumina pellets as inert material (catalyst particle size being 1 – 2 mm). The inner diameter of the reactor was 17 mm. The gas from the reactor was cooled down with cooling water. The water from the reactor was condensed and separated in a plastic container while the un-condensed gas was further streamed to a gas chromatography for

analysis. The composition of the inlet gas is presented in table 4 below. Steam-to-CO ratio was 2.8.

Table 4. The inlet gas composition (moist and dry) entering the reactor. The flow rates of the different components are presented as well.

Feed entering reactor	Moist gas [%]	Dry gas [%]	Flow-set in MFC
CO	10.8	15.4	6 L/h
CO <sub>2</sub>	16.2	23.1	9 L/h
H <sub>2</sub>	43.2	61.5	24 L/h
H <sub>2</sub> O	29.8	0	12.4 g/h

Gas chromatography was used to analyze the composition of the gas from the reactor. The CO conversion ( $X_{CO}$ ) was calculated according to the equation below (A):

$$X_{CO} = \frac{CO_{in} - CO_{out}}{CO_{in}} \quad (A)$$

The  $CO_{in}$  represents the initial CO concentration which was determined by taking a by-pass measurement with dry gas, while  $CO_{out}$  represents the CO concentration in the dry gas after the reactor. Gas chromatography was used to measure the CO and CH<sub>4</sub> content in all the performed experiments which are described down below.

### 3.3. Test plan

The activity, selectivity and stability of a catalyst is important for all catalytic applications. The aim of the performed experiments was to investigate in how the catalysts perform in terms of the activity, selectivity and stability during HT WGS conditions. The tests were divided into two parts; (1) short-term tests, and (2) long-term tests.

The aim of the performed short-term tests was to investigate the catalytic activity and selectivity. Fe/Cr and all the prepared catalysts were exposed to the short-term tests. The measurements were performed after 1 hour on-stream and at temperatures 350 °C, 400 °C, 450 °C and 500 °C. The activity and selectivity performance were determined by using gas chromatography to measure the CO and hydrocarbon concentration after the reactor. Low CO concentrations in the outlet gas and CO conversion near the equilibrium were desired and implied a great catalyst activity. Very low or no hydrocarbon products in the outlet gas implied great selectivity toward desired products, H<sub>2</sub> and CO<sub>2</sub>. The catalyst showing the best catalytic and selectivity performance was further analyzed in the long-term test.

The aim of the performed long-term test was to investigate the stability of the catalyst. The catalyst was put through HT WGS conditions for 135 hours and at reactor temperature 400 °C. Measurements were made every 12<sup>th</sup> hour in order to follow the catalyst activity and

eventual activity drops. All the tests, the short- and the long-term, were performed at atmospheric pressure.

#### 3.4. Catalyst characterization

Evaluation of surface areas was performed by the suggested equations by Brunauer, Emmet and Teller (BET). BET adsorption–desorption method using a Micromeritics 3-FLEX instrument (Norcross, GA, USA) was used to determine the specific surface area and pore size of the catalyst. Barrett, Joyner and Halenda (BJH) method was used for the analysis of pore volume. [35] Degassing of the sample was carried out at 250 °C under high vacuum for 4 h before the analysis. Measurements were conducted using nitrogen as the probe gas at liquid nitrogen temperatures. [36]

## 4. Results and discussion

In the following section, results from the catalyst characterisation, the short-term and the long-term tests are presented and discussed.

### 4.1. Catalyst characterization

In table 5, the BET surface area, pore volume and pore size for the supports and the prepared catalysts are presented.

Table 5. BET analysis of the supports and prepared catalysts for HT WGS catalysts.

	<b>BET surface area [m<sup>2</sup>/g]</b>	<b>Pore volume [cm<sup>3</sup>/g]</b>	<b>Pore size [Å]</b>
CeZrO <sub>2</sub>	110	0.206	76.3
TiO <sub>2</sub>	105	0.350	140
3%Pt/Re/CeZrO <sub>2</sub>	87	0.214	98.0
1.5%Pt/Re/CeZrO <sub>2</sub>	88	0.219	99.2
3%Pt/Re/TiO <sub>2</sub>	73	0.212	116.2
1.5%Pt/Re/TiO <sub>2</sub>	76	0.221	116.8
Cat. E	46	0.127	109.3
Cat. F	-	-	-

When comparing the different supports, the results show that the surface area is similar for both the CeZrO<sub>2</sub> and TiO<sub>2</sub> (110 and 105 m<sup>2</sup>/g, respectively). Furthermore, when adding the noble metal and a promoter or a dopant, the surface area of the catalyst is decreased. This applied to all the prepared catalysts in the experimental part. The most distinguishable catalyst is the Cat. E, which only has a surface area of 46 m<sup>2</sup>/g. The reduced surface area is most likely due to the alkali metal or the transition metal blocking the pores of the support. Cat. F was prepared at a later stage of the thesis project and due to the time limitation, the BET test on this catalyst was not executed.

### 4.2. Short-term tests

This part presents the activity and selectivity results in the performed short-term tests. The different catalyst formulations (Pt/Re/CeZrO<sub>2</sub>, Pt/Re/TiO<sub>2</sub> and Cat. E/Cat. F) are separately compared to the Fe/Cr catalyst. Based on the results, it is determined if a catalyst formulation is suitable for the HT WGS reaction and if it should be further analysed in the long-term stability test.

#### 4.2.1. Pt/Re/CeZrO<sub>2</sub> catalyst

The first catalysts which were tested in the system set-up was the Pt/Re supported on CeZrO<sub>2</sub> catalyst. In figure 7 and table 6, the CO conversion as a function of the temperature is presented for both Pt/Re/CeZrO<sub>2</sub> and Fe/Cr catalyst.

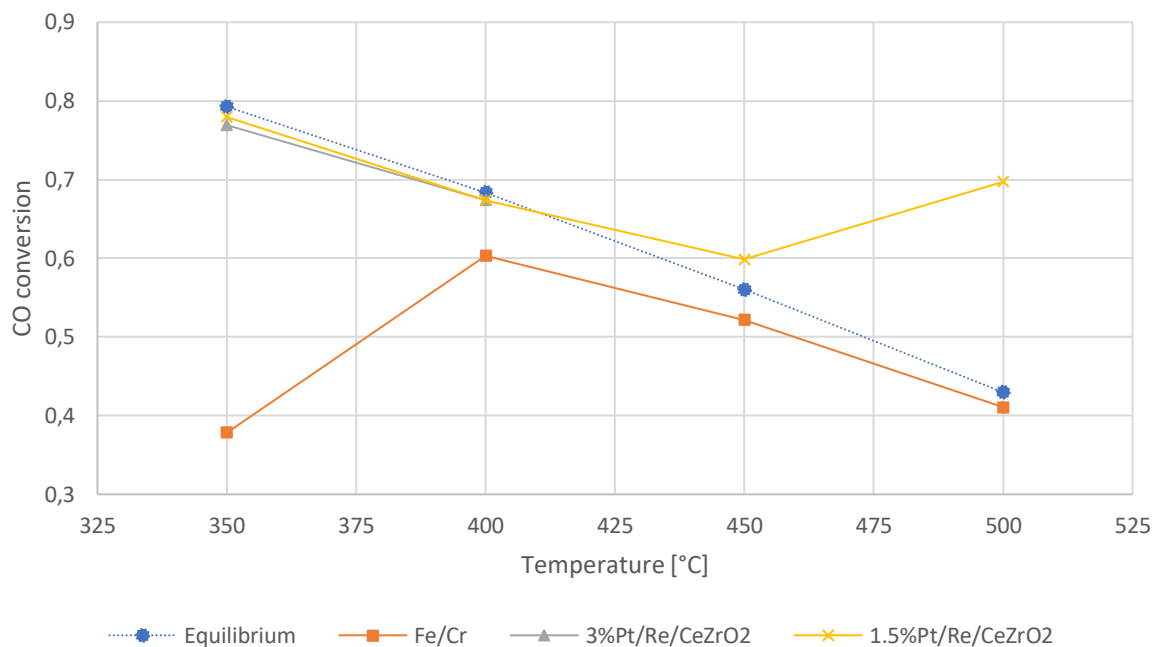


Figure 7. CO conversion for Fe/Cr (the orange line), 3%Pt/Re/CeZrO<sub>2</sub> (the black line) and 1.5%Pt/Re/CeZrO<sub>2</sub> (the yellow line) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

The results do show that the Pt/Re/CeZrO<sub>2</sub> catalysts are much more active compared to the Fe/Cr catalyst. However, at temperatures above 400 °C, the 1.5 wt.% Pt/Re/CeZrO<sub>2</sub> does rapidly exceed the equilibrium line. This clearly indicates that the CO is consumed to produce other products than the desired ones, CO<sub>2</sub> and H<sub>2</sub>. Due to temperature escalation in the reactor when using the 3 wt.% Pt/Re/CeZrO<sub>2</sub>, only two measurements were performed on the catalyst. Thus, only measurements at 350 °C and 400 °C are presented. However, the trend displayed by the 1.5 wt.% Pt/Re/CeZrO<sub>2</sub> catalyst suggests that the catalyst containing a larger concentration of active phase would also exceed the equilibrium line at temperatures above 400 °C.

Table 6. CO conversion using Fe/Cr and Pt/Re/CeZrO<sub>2</sub> catalysts. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	CO conversion [%]			
	350 °C	400 °C	450 °C	500 °C
<b>At equilibrium</b>	79.3	68.4	56.0	43.0
<b>Fe/Cr</b>	37.8	60.3	52.2	41.1
<b>3%Pt/Re/CeZrO<sub>2</sub></b>	76.9	67.4	-	-
<b>1.5%Pt/Re/CeZrO<sub>2</sub></b>	77.9	67.4	59.9	69.8



The CO conversion for Pt/Re/CeZrO<sub>2</sub> catalysts shows that the CO is consumed to other products than the desired H<sub>2</sub> and CO<sub>2</sub>. It is well-known that noble based metals supported on partially reduced oxides do catalyse methane. This fact is confirmed by the results from the gas chromatography measurements, detecting methane produced using the Pt/Re/CeZrO<sub>2</sub> catalysts. The results showing methane production for Pt/Re/CeZrO<sub>2</sub> and Fe/Cr catalysts are presented in figure 8 and table 7.

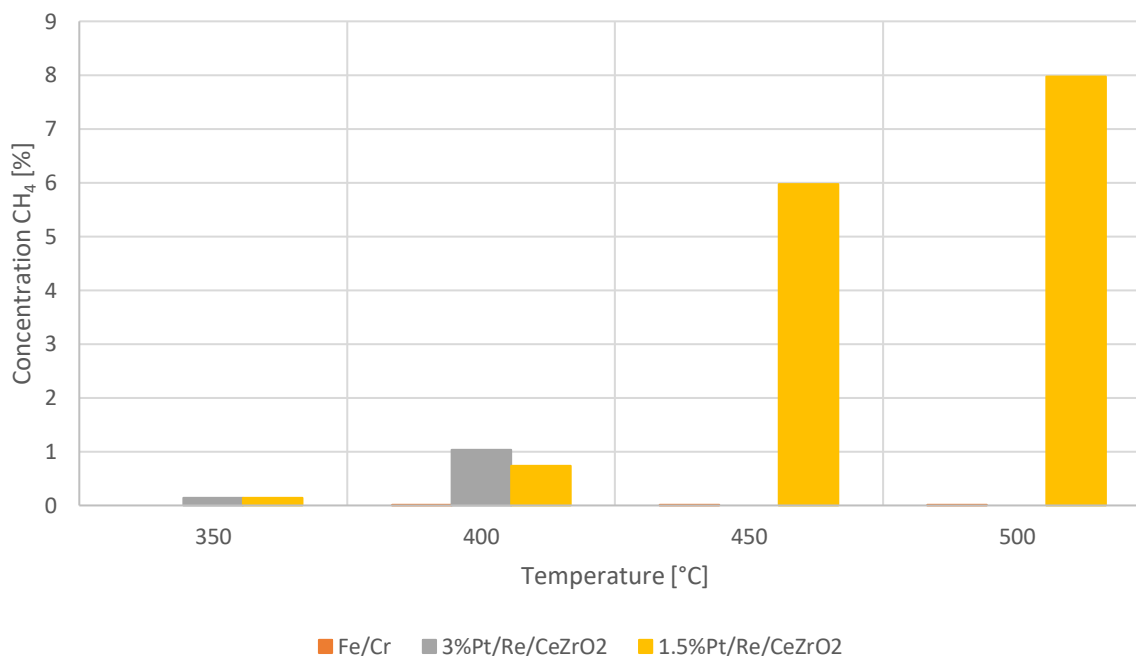


Figure 8. CH<sub>4</sub> formation after the reactor using Fe/Cr (the orange bar), 3%Pt/Re/CeZrO<sub>2</sub> (the black bar) and 1.5%Pt/Re/CeZrO<sub>2</sub> (the yellow bar) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>. Only two measurements were performed (350°C and 400°C) using 3%Pt/Re/CeZrO<sub>2</sub> catalyst.

The methane formation increases with increased temperature for both Pt/Re/CeZrO<sub>2</sub> catalysts. In comparison, Fe/Cr catalyst does not show any or very low methane formation in this temperature interval compared to Pt/Re/CeZrO<sub>2</sub> catalysts. Because of the high methane formation, it was concluded that the Pt/Re/CeZrO<sub>2</sub> catalyst formulation is not appropriate for the HT WGS reaction. In order to be functioning as a HT WGS catalyst, the formulation needs to be modified and have the ability to suppress methane formation. Further stability test was therefore not performed on these formulations.

Table 7. Methane production using Fe/Cr, 3 wt.% Pt/Re/CeZrO<sub>2</sub> and 1.5 wt.% Pt/Re/CeZrO<sub>2</sub> catalysts. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed was 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	Methane production [vol. %]			
	350 °C	400 °C	450 °C	500 °C
<b>Fe/Cr</b>	0.0000	0.0020	0.0028	0.0057
<b>3%Pt/Re/CeZrO<sub>2</sub></b>	0.1386	1.037	-	-
<b>1.5%Pt/Re/CeZrO<sub>2</sub></b>	0.1441	0.7336	5.9717	7.976

#### 4.2.2. Pt/Re/TiO<sub>2</sub> catalyst

In order to answer the second research question, the Pt/Re supported on TiO<sub>2</sub> was installed in the system set-up. Figure 9 and table 8 presents the results from the gas chromatography measurements performed on the Pt/Re/TiO<sub>2</sub> and Fe/Cr catalysts. The CO conversion is plotted as a function of the temperature.

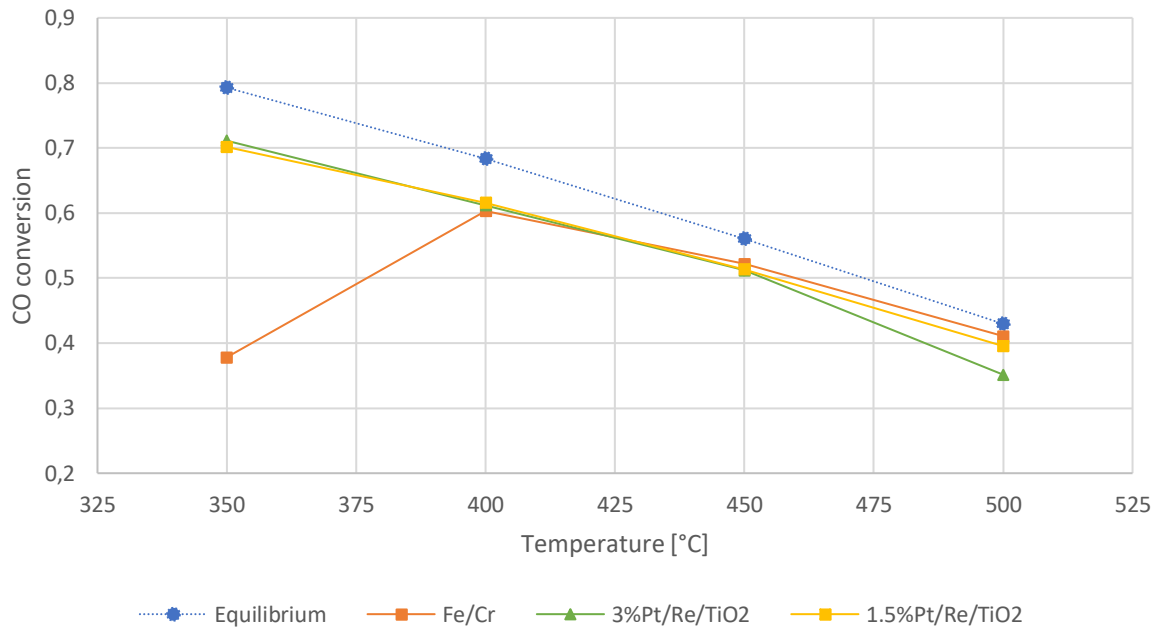


Figure 9. CO conversion for Fe/Cr (the orange line), 3%Pt/Re/TiO<sub>2</sub> (the black line) and 1.5%Pt/Re/TiO<sub>2</sub> (the yellow line) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

The results show that the Pt/Re/TiO<sub>2</sub> catalysts exhibit higher activity compared to the Fe/Cr catalyst. According to the graph, the ignition curve for both Pt/Re/TiO<sub>2</sub> catalysts seems to occur at temperatures below 350 °C. However, measurements at lower temperatures should be performed in order to confirm this. An interesting note is that the CO conversion for both the 3 wt.% Pt/Re/TiO<sub>2</sub> and the 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalysts are close to identical, despite the latter catalyst containing half as much of the active phase. It could depend on the surface area and how the Pt is dispersed on the catalyst. Lower concentrations of metal on the surface area may give a better dispersion and smaller metal clusters. [4] Therefore, more active sites will be available for the reactant gas, resulting in higher catalytic activity. On the other hand, it is known that the smaller metal clusters on a catalyst surface area are less stable than the larger clusters. The smaller clusters will therefore sinter faster when exposed to high temperatures, deactivating the catalyst. If the assumption about the dispersion is correct, there is a risk that the 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalyst will sinter much more rapidly than the 3 wt.% Pt/Re/TiO<sub>2</sub> catalyst when exposed for to the HT WGS reaction conditions during a long period of time. However, to confirm this theory, measurement on Pt particles of the catalyst should be performed.

Table 8. CO conversion using Fe/Cr, 3 wt.% Pt/Re/TiO<sub>2</sub> and 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalysts. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	CO conversion [%]			
	350 °C	400 °C	450 °C	500 °C
<b>Equilibrium</b>	79.3	68.4	56.0	43.0
<b>Fe/Cr</b>	37.8	60.3	52.2	41.1
<b>3%Pt/Re/TiO<sub>2</sub></b>	71.0	61.2	51.2	35.1
<b>1.5%Pt/Re/TiO<sub>2</sub></b>	70.0	61.6	51.3	39.5

Even though the CO conversion does not exceed the equilibrium, it cannot be concluded that the catalysts are selective towards the desired products, H<sub>2</sub> and CO<sub>2</sub>. The collected results show that methane was produced using Pt/Re/TiO<sub>2</sub> catalysts. However, if compared to the Pt/Re/CeZrO<sub>2</sub>, significantly lower concentrations were detected. The results are presented in figure 10 and table 9.

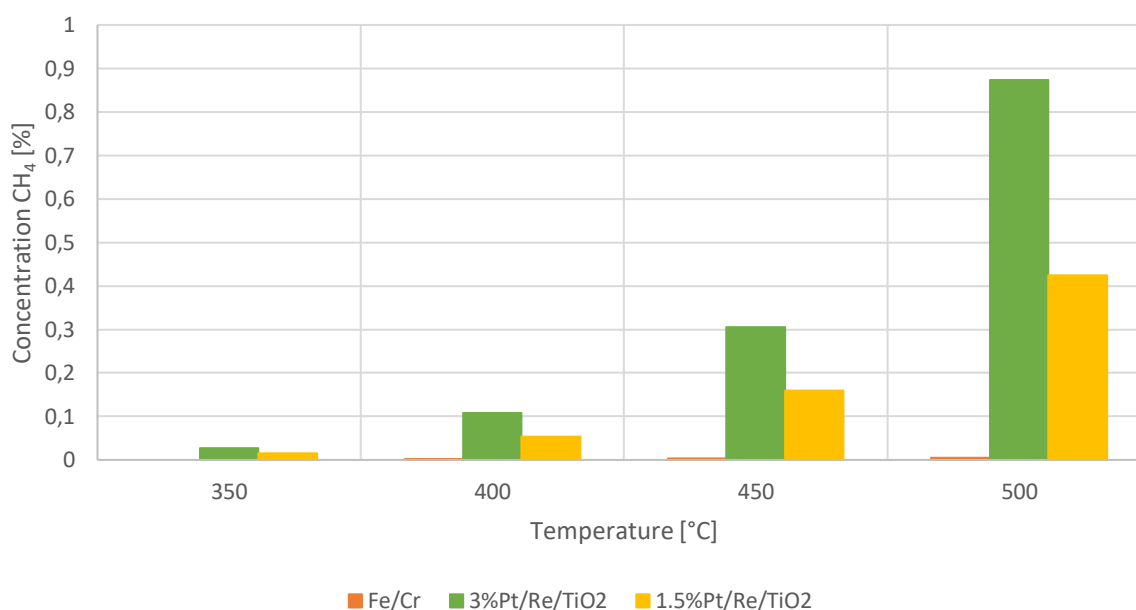


Figure 10. CH<sub>4</sub> formation after the reactor using Fe/Cr (the orange bar), 3%Pt/Re/TiO<sub>2</sub> (the black bar) and 1.5%Pt/Re/TiO<sub>2</sub> (the yellow bar) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>. Only two measurements were performed (350°C and 400°C) using 3%Pt/Re/CeZrO<sub>2</sub> catalyst.

Comparing the methane production using the commercial Fe/Cr catalyst and the Pt/Re/TiO<sub>2</sub>, it can be concluded that the latter catalysts produce significantly more methane. Another interesting note is that when less Pt is used, the 1.5 wt.% Pt catalyst produces about half as much methane compared to 3 wt.% Pt catalyst. These results, together with the activity measurements, imply that the 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalyst is more selective than the 3 wt.% Pt/Re/TiO<sub>2</sub> catalyst. The difference in the methane production between the catalyst may depend on the dispersion of the Pt on the surface of the catalyst. When less Pt is used, the

particles are smaller and more dispersed over the area. To produce a CH<sub>4</sub> molecule, there must be one active site for the CO to adsorb on and at least three active sites nearby to adsorb the H<sub>2</sub>. In the case of 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalyst, an equal dispersion of the Pt would mean that the active sites have a longer distance to each other, compared to the 3 wt.% Pt/Re/TiO<sub>2</sub> catalyst. This could explain the lower amount of methane being produced. However, in order to confirm this theory, an analysis of the particle sizes and distance is required.

Table 9. Methane production using Fe/Cr, 3 wt.% Pt/Re/TiO<sub>2</sub> and 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalysts. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed was 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	<b>Methane production [vol.%]</b>			
	<b>350 °C</b>	<b>400 °C</b>	<b>450 °C</b>	<b>500 °C</b>
<b>Fe/Cr</b>	0.0000	0.0020	0.0028	0.0057
<b>3%Pt/Re/TiO<sub>2</sub></b>	0.0265	0.1077	0.3052	0.8738
<b>1.5%Pt/Re/TiO<sub>2</sub></b>	0.0147	0.0593	0.1593	0.4251

Another interesting result is that a support change from CeZrO<sub>2</sub> to TiO<sub>2</sub> significantly decreases methane formation. This confirms that the support plays a significant role in the catalyst formulation.

Based on the results showing the high methane formation, it is determined that the Pt/Re/TiO<sub>2</sub> catalysts are not suitable for HT WGS reaction, despite showing better performance in this regard than that of the CeZrO<sub>2</sub> catalysts. Therefore, these catalysts were not further studied in the long-term stability test.

#### 4.2.3. Cat. E/Cat. F

To answer the third research question, the Pt promoted with an alkali metal and a transition metal supported on CeZrO<sub>2</sub> was installed in the system set-up. Figure 11 presents the results from the gas chromatography measurements performed on Cat. E, Cat. F and Fe/Cr catalysts. The CO conversion is plotted as a function of the temperature.

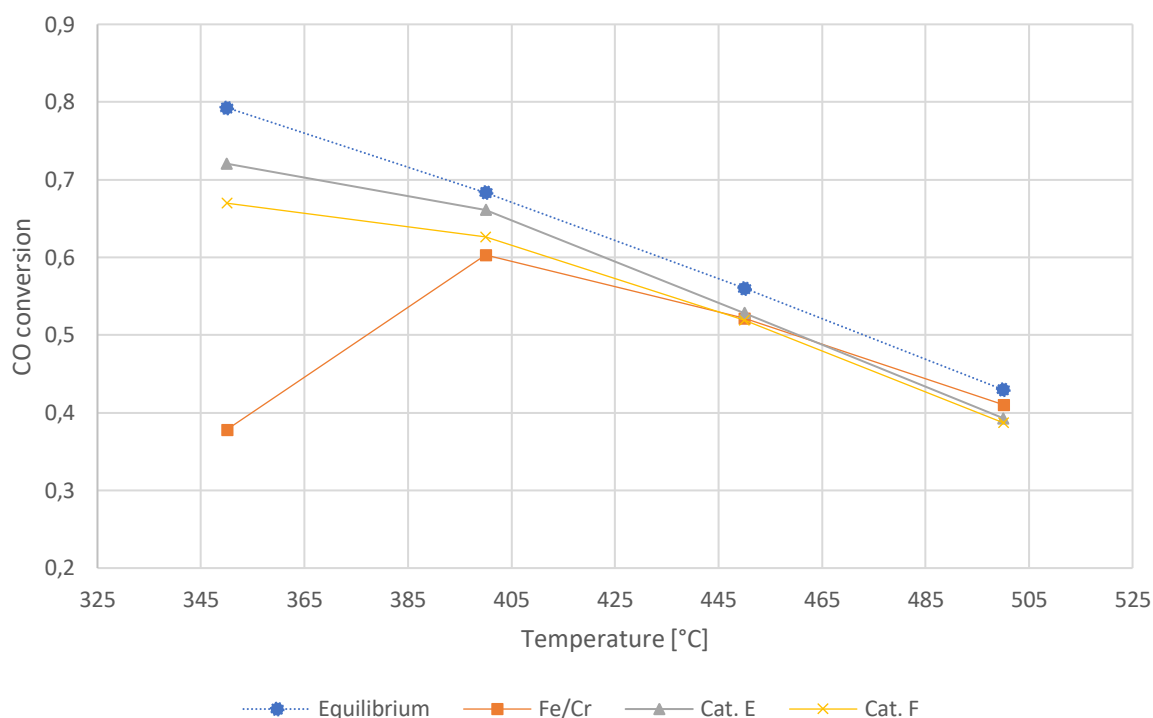


Figure 11. CO conversion for Fe/Cr (the orange line), Cat. E (the grey line) and Cat. F (the yellow line) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

The results show that the prepared catalysts show significantly higher activity compared to the Fe/Cr catalyst. According to the graph, the ignition curves for both E and F catalysts seem to occur at temperatures below 350 °C. In order to confirm this assumption, measurements at temperatures below 350 °C are required. Catalyst E exhibit higher CO conversion and, according to the results, is more active than the F catalyst. Table 10 presents CO conversion for these catalysts. Furthermore, the methane production for these catalyst formulations is presented in figure 12 and table 11.

Table 10. CO conversion using Fe/Cr, Cat. E and Cat. F. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	CO conversion [%]			
	350 °C	400 °C	450 °C	500 °C
<b>Equilibrium</b>	79.3	68.4	56.0	43.0
<b>Fe/Cr</b>	37.8	60.3	52.2	41.1
<b>Cat. E</b>	72.0	66.1	52.9	39.3
<b>Cat. F</b>	67.0	62.7	51.9	38.7

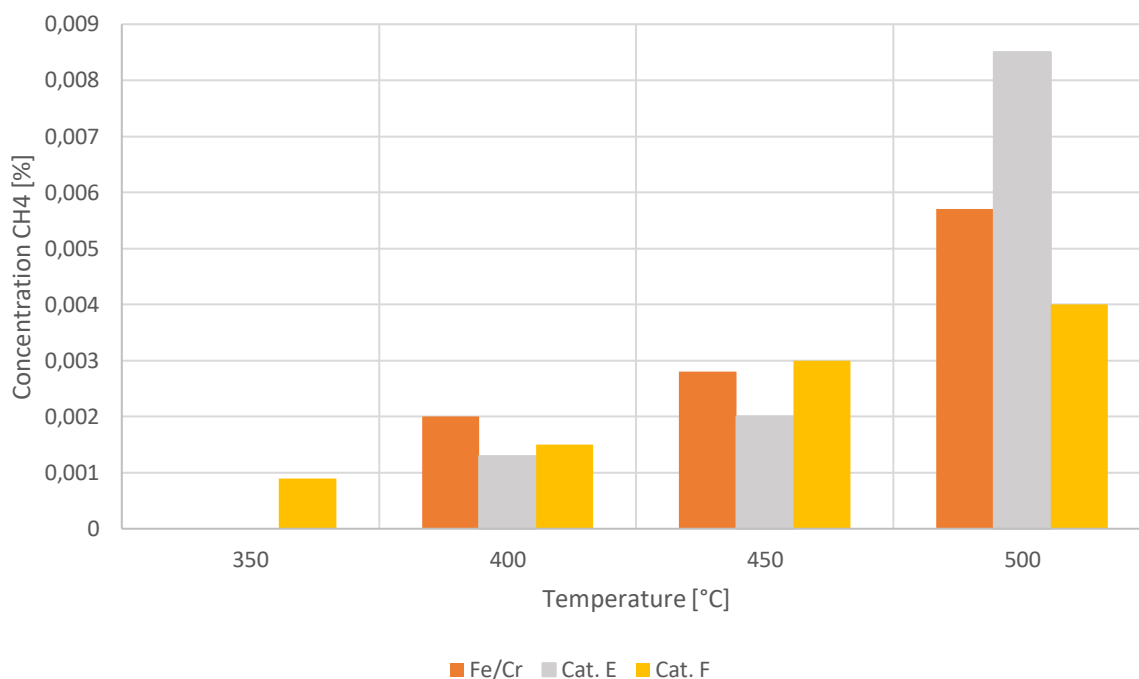


Figure 12. CH<sub>4</sub> formation after the reactor using Fe/Cr (the orange bar), Cat. E (the grey bar) and Cat. F (the yellow bar) are presented in the figure. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

Insignificant or extremely low concentrations of methane were detected during the experiments for the E and F catalysts. As the gas chromatography detector has a noise threshold of 0.002 %, the methane measurements below this value are insignificant. Thus, it is confirmed that methane formation is present at temperatures at or above 450 °C for the catalysts E and F, and temperatures at or above 400 °C for the Fe/Cr catalyst. Comparing the methane formation of the commercial Fe/Cr catalyst, the results show that similar and very low concentrations of methane are produced in the reactor when using E and F catalysts.

Table 11. Methane production using Fe/Cr, Cat. E and Cat. F. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

	Methane production [vol.%]			
	350 °C	400 °C	450 °C	500 °C
<b>Fe/Cr</b>	0.0000	0.0020	0.0028	0.0057
<b>3%Pt/Fe/K<sub>2</sub>O/CeZrO<sub>2</sub></b>	0.0000	0.0013	0.0020	0.0085
<b>1.5%Pt/Fe/K<sub>2</sub>O/CeZrO<sub>2</sub></b>	0.0009	0.0015	0.0030	0.0040

The addition of the alkali and transition metals does improve the catalyst performance significantly, both in terms of activity and selectivity. In fact, by replacing the Re promoter with an alkali metal and a transition metal, the methane production is decreased by nearly

99.9% (when comparing the methane production of the 1.5 wt.% Pt/Re/CeZrO<sub>2</sub> and Cat. F at 500 °C).

Based on the promising short-term results, both E and F catalyst formulations are considered to be excellent candidates for further long-term stability tests. However, because of the time limitation, only one could be chosen to be further analysed in this thesis project. Both formulations produced no or very low amounts of methane, although, methane production was significantly lower at 500 °C when using Cat. F. However, as the HT WGS usually operates at temperatures 310-450 °C, the results measured at 500 °C were disregarded. In terms of the activity, Cat. E perform better, and therefore, this catalyst was chosen to be further studied in the long-term stability test.

#### 4.3. Long-term experiment with catalyst E

Catalyst E was exposed for HT WGS reaction conditions for 135 hours, and activity measurements were performed every 12<sup>th</sup> hour. Figure 13 presents CO conversion as a function of time is presented.

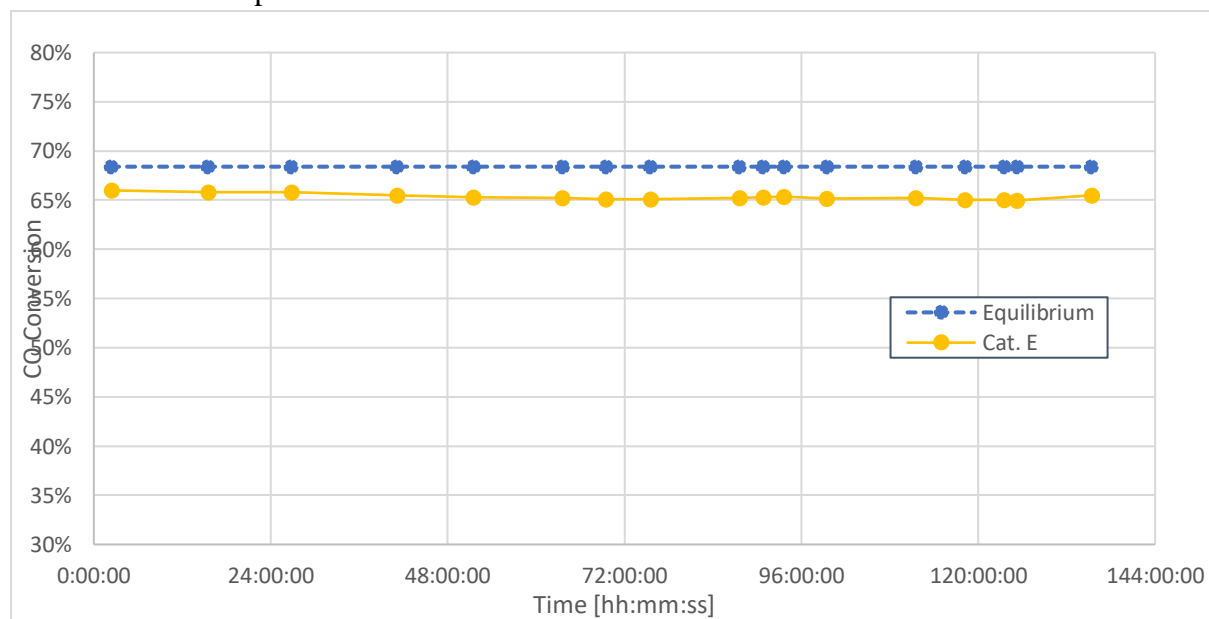


Figure 13. CO conversion during the long-term test with Cat. E. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>. The preheater and reactor temperatures were set to 400 °C.

The results show that the catalyst is active and stable during the entire long-term test period. The first measurement was performed 2 hours after the feed was introduced to the system and showed 66 % CO conversion (compared to the equilibrium line where the CO conversion is 68.4%). No activity drop is detected during this time, indicating that the catalyst is resistant towards the deactivation mechanisms such as sintering of the metal and the support, and over-reduction of the CeZrO<sub>2</sub>.

Figure 14 show the concentration of CO and CH<sub>4</sub> in the outlet gas. The concentration is presented as a function of time.

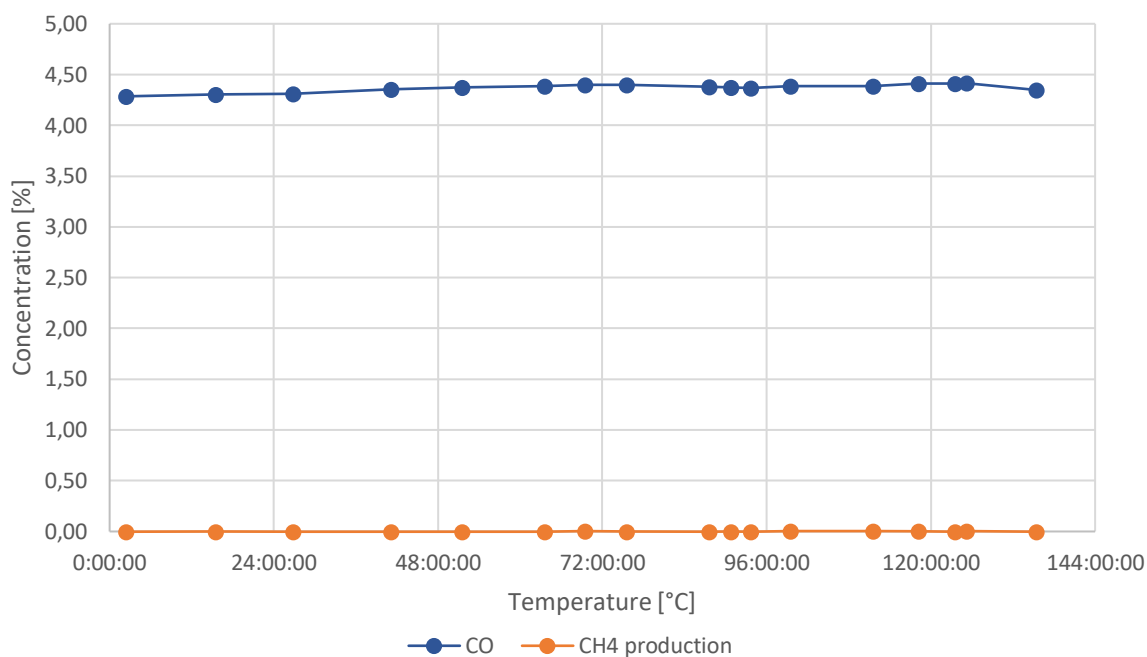


Figure 14. CO and CH<sub>4</sub> concentrations in the outlet gas during the long-term test with Cat. E. The operation conditions during measurements were GHSV: 20.000 h<sup>-1</sup>. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>. The preheater and reactor temperatures were set to 400 °C.

The results show no methane formation during the entire long-term test period, for at least 135 hours. The stability results indicate that the catalyst shows excellent performance in the terms of activity, selectivity, and stability. Once the long-term stability test was performed and the catalyst had aged, the catalytic activity was again measured for all the temperatures, 350 – 500 °C. In figure 15, CO conversion of fresh and aged catalysts are presented and compared.



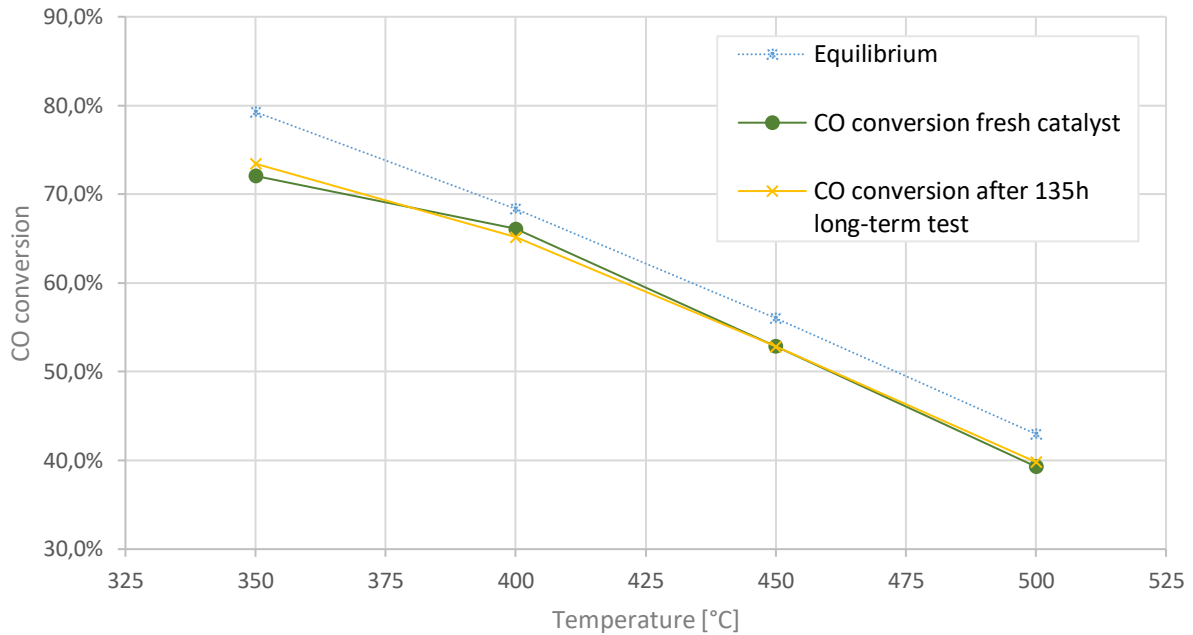


Figure 15. CO conversion with fresh/used Cat. E. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

The aim of measuring the catalyst after the long-term test is to detect if any decrease in the catalytic activity occurs. The results show that no decrease is occurring after 135 hours on-stream. In fact, the catalyst seems to perform slightly better after being exposed to HT WGS conditions for a long time. The stability results are surprising and impressive, considering the low surface area of the catalyst.

Methane production was also measured and compared after the long-term test, and the results are presented in figure 16.

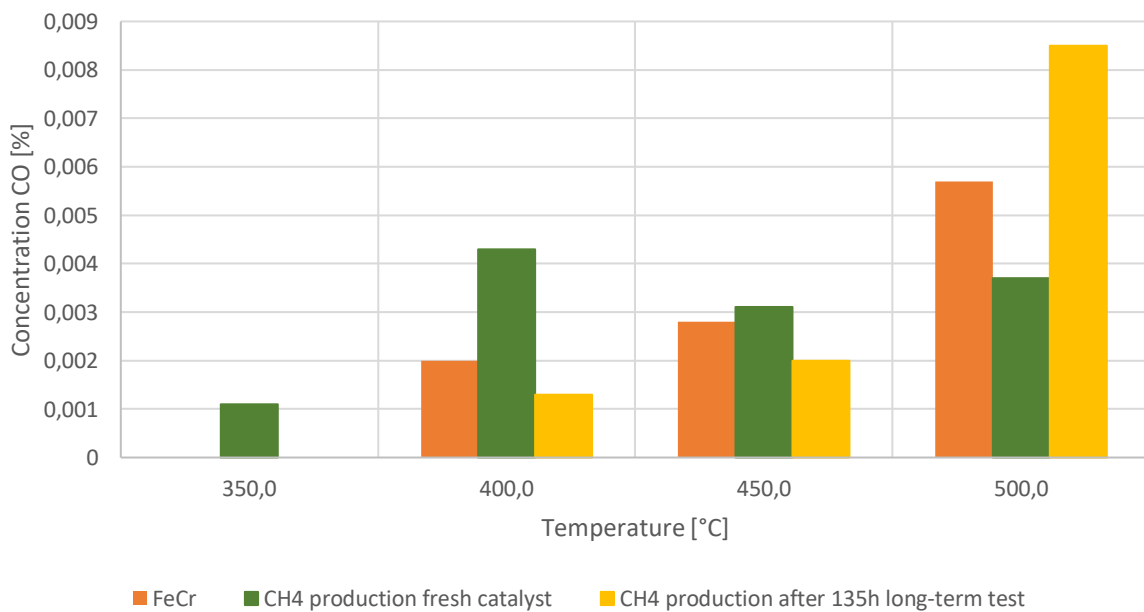


Figure 16. CH<sub>4</sub> formation fresh/used Cat. E. The measurements were performed at ambient pressure and a GHSV of 20,000 h<sup>-1</sup>. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

The results show that the methane formation is kept at very low concentrations, even after the catalyst is aged. This implies that the catalyst selectivity towards desired products, H<sub>2</sub> and CO<sub>2</sub> does not change after 135 hours. Detection below 0.002 % is assumed to be noise in analysis instrument.

#### 4.3.1. Conversion with varied GHSV

In order to investigate the catalytic activity during representative industrial conditions, the catalyst was tested at lower space velocities; 3000 h<sup>-1</sup> and 5000 h<sup>-1</sup>. Decreasing the GHSV, gives the reactants more time to be exposed to the catalyst, and therefore, an increased conversion is expected. In figure 17, the CO conversion using different space velocities are presented.

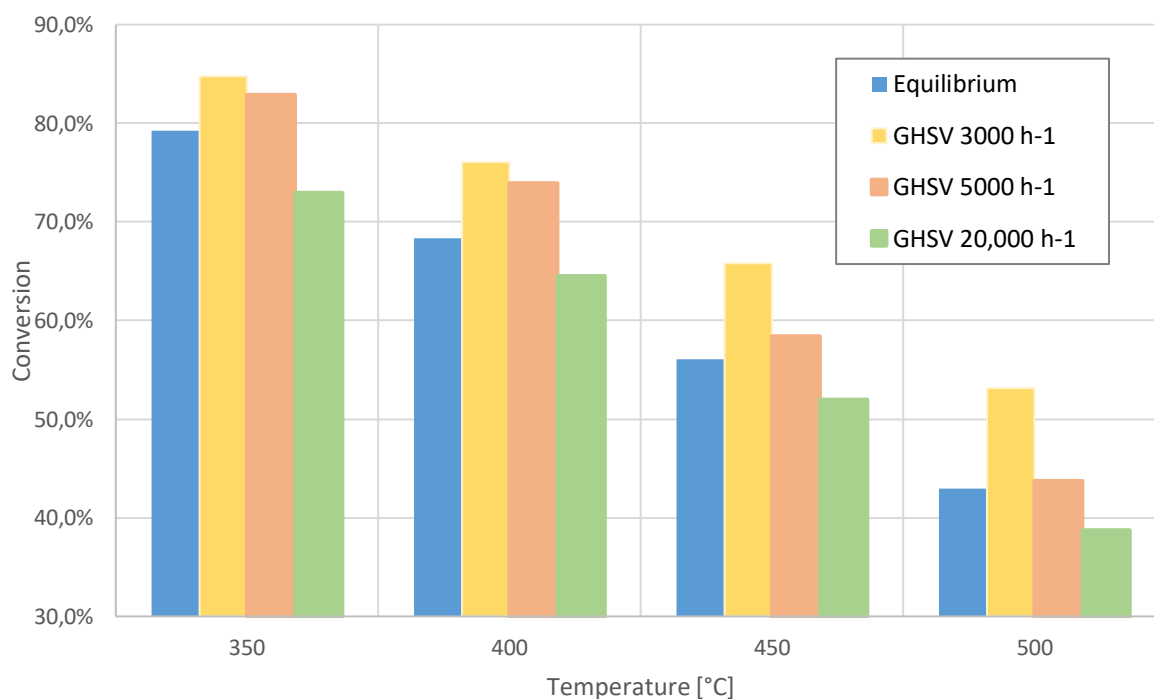


Figure 17. CO conversion of Cat. E using different GHSV. The measurements were performed at ambient pressure. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

As seen in figure 18, the CO conversion exceeds the equilibrium in the measurements where GHSV is 3000 h<sup>-1</sup> and 5000 h<sup>-1</sup> for all the measured temperatures. In the first place, it was thought that the CO was consumed to produce CH<sub>4</sub>, however, only small traces of methane were detected in the gas chromatography. No other hydrocarbon products were noted in the reactor outlet. The reason for the high CO conversion at low GHSV is thought to be due to the unstable water input into the reactor. Since the water flow was very low at these space velocities, the water input would variate +/- 5%. Most likely, the measurements were taken with a higher steam/CO ratio than calculated. It should also be noted that the equilibrium was calculated for the precise temperatures (350 °C, 400 °C, 450 °C, 500 °C), while the real-life reactor average temperature was varying up to 10 °C during the experiment due to the

reaction being exothermic. Methane formation at different space velocities is presented in figure 18 and table 12.

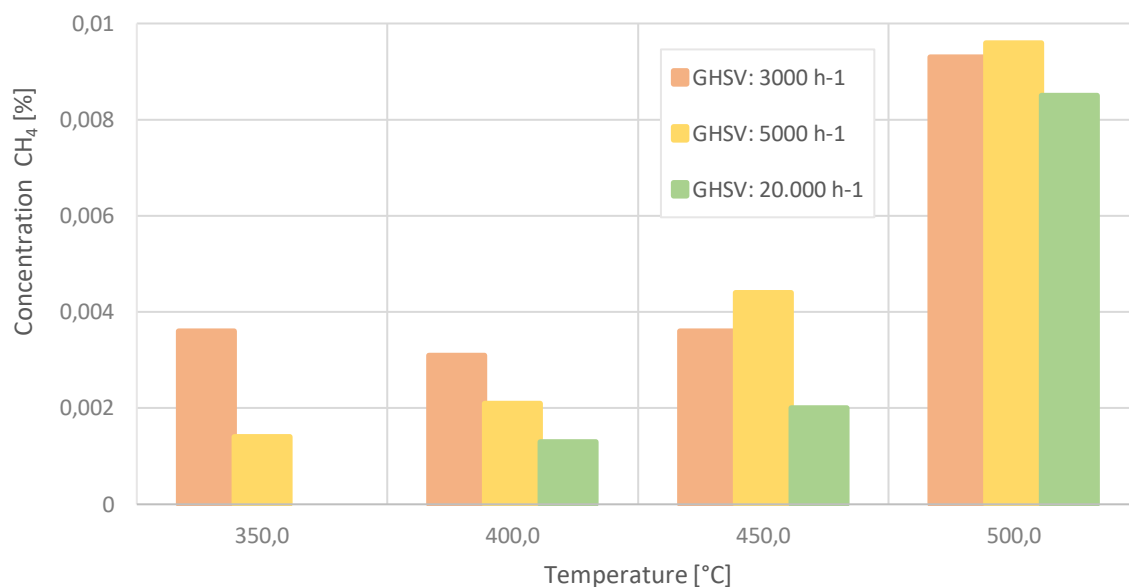


Figure 18. CH<sub>4</sub> formation of Cat. E using different GHSV. The measurements were performed at ambient pressure. The reactor feed consisted of 10.8% CO, 29.8% H<sub>2</sub>O, 43.2% H<sub>2</sub> and 16.2% CO<sub>2</sub>.

A small increase in methane production occurs when space velocities are lowered. However, it is concluded that the catalyst is still selective, even at low GHSV.

Table 12. Methane formation using catalyst E at different space velocities.

	<b>Methane production [%]</b>			
	<b>350 °C</b>	<b>400 °C</b>	<b>450 °C</b>	<b>500 °C</b>
<b>GHSV: 20,000 h<sup>-1</sup></b>	0.0000	0.0013	0.0020	0.0085
<b>GHSV: 5000 h<sup>-1</sup></b>	0.0014	0.0021	0.0044	0.0096
<b>GHSV: 3000 h<sup>-1</sup></b>	0.0036	0.0031	0.0036	0.0093



## 5. Conclusion

This thesis project shows that the choice of dopants and the support plays a crucial role in the catalytical activity, selectivity and stability performance. By replacing the support or adding dopants in a catalyst formulation, the selectivity towards the desired products can be significantly increased. The performed experiments in this thesis project show that the performance of the Pt/Re/CeZrO<sub>2</sub> catalyst was improved when modifying the formulation. The collected results enabled to answer the research questions asked in the introduction:

(1) Is the Pt/Re catalyst supported on CeZrO<sub>2</sub> also suitable for HT WGS applications?

No, the Pt/Re/CeZrO<sub>2</sub> is not suitable for the high-temperature water-gas shift reaction. Both 3 wt.% and 1.5 wt.% Pt/Re/CeZrO<sub>2</sub> perform poorly in terms of selectivity when operated at the HT WGS conditions. At temperatures 350 °C and above, the catalysts produce high concentrations of methane, which is an un-desired product for WGS reaction.

(2) Does changing the support of Pt/Re/CeZrO<sub>2</sub> change the activity, selectivity, and stability of the catalyst?

The support was changed from CeZrO<sub>2</sub> to TiO<sub>2</sub>. The activity and selectivity for the catalyst was significantly improved when changing the support. The methane productions for all measured temperatures was decreased when using the Pt/Re/TiO<sub>2</sub> catalysts. When compared to the commercial Fe/Cr catalyst, both the 3 wt.% and 1.5 wt.% Pt/Re/TiO<sub>2</sub> catalysts exhibit higher activities. However, the methane production is significantly higher for the Pt/Re/TiO<sub>2</sub>. Due to not being as selective as the commercial Fe/Cr catalysts, the stability of the formulations was never investigated.

(3) Does changing the promoter of Pt/Re/CeZrO<sub>2</sub> catalyst improve the activity, selectivity, and stability of the catalyst?

By replacing the Re in the Pt/Re/CeZrO<sub>2</sub> catalyst to an alkali and a transition metal, the catalyst performance was significantly improved in terms of both the activity and selectivity. The catalysts exhibit high CO conversion at all measured temperatures (350 – 500 °C) and produces none or very low methane concentrations during the operating conditions in the experiments. The long-term stability test was performed on the catalyst E. It is difficult to answer if the stability of the catalyst was improved or not. Because of the high methane formation, Pt/Re/CeZrO<sub>2</sub> was never studied in the long-term test and therefore, the results do not exist to compare the catalysts. It is known from the literature that the initial deactivation usually occurs after 50 – 100 hours on-stream. Since the catalyst was stable for over 135 hours, it is concluded that the stability is very impressive. During the long-term test performed at temperature 400 °C, the catalyst exhibited 66 % CO conversion (maximum CO conversion is 68.4 % at 400 °C due to equilibrium) and lost only 0.5 % (65.5% CO conversion on the last measurement) during the 135-hour test.

### 5.1. Future work

The successful results show that the catalyst E is a highly promising candidate for the HT WGS applications. However, further work is needed to be done in order to confirm the catalytical performance during other operating conditions than those performed in this thesis project. For catalyst E, it is suggested that the future work should include:

- Performing experiments on the catalyst during pressurized conditions. Since the HT WGS reaction is usually operating at high pressures, the catalyst behaviour should be investigated during those conditions as well. Also, methane production is favoured when pressure is increased. Therefore, measuring the methane concentrations at different pressures are of significant interest.
- Performing experiments with lower steam-to-CO ratios in order to investigate the catalyst stability during more extreme conditions.
- Analysing the aged catalyst by BET in order to measure eventual changes in the surface area.
- Economic analysis in order to investigate if the catalyst price is competitive against the Fe/Cr catalyst and the other HT WGS catalysts on the market.

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