Evaluation of Non-Noble Metal Catalysts for CO Oxidation

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Abstract

The aim of the study is to evaluate the ability of non-noble metal catalysts to function as the commercially used noble metal catalyst. The exhaust gas that was used in the project is generated from a heater developed by ReformTech with diesel as fuel. The compound that was focused on is carbon monoxide that has a concentration of 300-750 ppm. The catalysts that were tested are MnO/CeO$_2$, CuO/CeO$_2$ and a Pt/CeO$_2$ catalyst used to compare the non-noble metal catalyst with. The sensitivity against sulfur poisoning was also analysed by mixing sulfur into the fuel. Analysis of the exhaust gas was done with a micro-GC and the catalysts were also analysed with SEM before and after exposure of sulfur.

The manganese catalyst with a loading of 7 wt-% did not show any activity against carbon monoxide oxidation. The copper catalysts contained two different loadings of active material, 7 and 14 wt-% and monoliths with 400 and 600 cpsi were used. Both loadings showed good activity against carbon monoxide oxidation.

The most prominent catalyst was the 14 wt-% CuO/CeO$_2$ catalyst with a 600 cpsi monolith because of an increase in surface area. The SEM analysis showed that sulfur was present on the surface when the heater was using diesel with 300 ppm sulfur. The sulfur caused complete deactivation of the non-noble metal catalysts and a small decrease in activity was shown on the noble metal Pt catalyst.
Sammanfattning


Mangankatalysatorn med 7 wt-% visade ingen aktivitet mot kolmonoxid oxidation. Kopparkatalysatorn testades med två olika koncentrationer aktivt material, 7 och 14 wt-% och monoliter med 400 och 600 cpsi användes. Både 7 och 14 wt-% katalysatorerna var aktiva mot kolmonoxid oxidering.

Den katalysatorn som visade sig vara bäst för kolmonoxid oxidation var CuO/\(\text{CeO}_2\) med monoliten med 600 cpsi på grund av den ökade ytarea som uppstår. SEM analyserna visade att svavel fanns på katalysatorytan efter att värmaren använt diesel innehållande 300 ppm svavel. Svavlet orsakade total deaktivering av icke-ädelmetall katalysatorerna och en liten deaktivering på ädelmetall katalysatorn.
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1 Introduction

Today’s regulations are tightening the limits of emissions so the requirements of the catalyst in a engine are increasing. The Euro 5 and Euro 6 regulations limits the emissions of carbon monoxide to be below 0.5 g/km for passenger cars. Considering the increasing awareness on these emission standards continuous development of efficient and cheap catalyst are required. [1] The heater that was used for testing non-noble-metal catalysts is developed by ReformTech, a company developing diesel heaters for applications such as passenger cars, buses and boats. The main reasons for ReformTech to develop these heaters are economical and environmental point of view. The Euro 6 drives the environment limitations which makes it important to develop low emission and efficient heaters. At the same time it important to develop a product that can be introduced into the market at reasonable costs. Since there are some competitors in the same area the costs are always an important factor to compete with other developers. The commercial catalyst in the heaters are based on noble-metals, such as platinum and palladium which are very effective towards reduction of pollutants such as CO. The main drawback with these catalysts is the high price which makes it interesting to find a catalyst based on non-noble-metals that could reduce the cost of the catalyst.

1.1 Aim and Goals

Previous work in this subject has been done where the focus was to find a non-noble catalyst with the ability to reduce the amounts of carbon monoxide in the exhaust gas. It was found that a copper oxide catalyst on ceria oxide showed the most prominent ability against carbon monoxide reduction. The aim in this project was to use the most efficient catalysts from the previous works and apply them in long term tests and the sensitivity against sulfur poisoning. The commercial catalyst was used as a comparison with the non-noble catalyst.

1.2 Limitations

- Previously prepared catalyst were used in this work which means that the catalyst composition could not be influenced.

- The composition of the exhaust gas could vary from day to day which has a small impact on the results.

- The produced catalysts were only designed in the mean of carbon monoxide reduction, whereas other impurities were not taken into account.

- The temperature of the exhaust gas varied slightly, a variation of about ±2% were observed during the tests.
2 Combustion

Combustion has been the main source of energy for a long time. It can be either controlled, the reaction takes place in a internal combustion engine where the air and fuel intakes are optimized, or uncontrolled where it is ignited with a fire or ignition source.

![Figure 1: The heater system developed by ReformTech [2]](image)

The purpose of the system in figure 1 is to heat up the water circulating in the system by heat exchange. A fan is controlling the intake of air into the system. The nozzle creates a finely dispersed spray of diesel which gives a more even combustion and lowering the emissions. Ignition of the fuel is done by the glow plug placed right after the nozzle. The water is circulating outside the reaction chamber while heat exchanging and leaves the system at a higher temperature. The parameters that are mainly controlled in the system are the air to fuel ratio and the fuel rate. The fuel rate is controlled by pressure and the air to fuel ratio is adjusted by changing the fan speed so that the desired air to fuel ratio is reached. The catalyst position can either be inside the reactor or outside in the exhaust gas pipe. In this project the catalyst was placed in the exhaust gas pipe for an easier management and exchange of catalyst.

2.1 Air to Fuel Ratio

The air to fuel ratio, $\lambda$, is an important parameter for a combustion engine. It is defined as $\frac{\text{mass air}}{\text{mass fuel}}$ ratio that enters the engine. If $\lambda$ is stoichiometric it means that the ratio between air and fuel is correct for an complete combustion, this stoichiometric condition represent a $\lambda$ of 14.7. $\lambda$ can also cause lean or rich conditions, which means that lambda is higher or lower than the stoichiometric $\lambda$. If $\lambda < 14.7$ results in a rich mixture with less air. And if $\lambda > 14.7$ the mixture is lean and contains more air. A higher combustion temperature is the result of a lean mixture. [3] $\lambda$ also effects the emissions of a engine. Figure 2 shows how the emissions of some common pollutants may vary with $\lambda$. 

2
2.2 Diesel

Diesel consists of hydrocarbons from $C_{10}$ up to $C_{22}$. Diesel is prepared from crude oil as raw material prepared from oil refineries. The emissions from a diesel engine are mainly NOx, SOx, CO and soot. Compared to a gasoline engine the emissions of CO for a diesel engine is much lower and the content of sulfur in the diesel fuel has decreased due to regulations the past years. The maximum allowed concentration of sulfur in commercially fuel diesel in Sweden according to MK1 is 10 ppm, but the concentration is usually below 5 ppm [5]. But there are still emissions that mainly are being reduced with a catalyst. The diesel combustion is a source of soot in the atmosphere consisting of carbon, unburned fuel and inorganic oxides. These soot particles can cause severe damage on humans and cause cancer or damage the heart and lungs.

3 Catalysts

Catalysts in today’s industrial processes are critical from an economical, environmental and efficiency point of view. The function of the catalyst is to reduce the amount of pollutants for example in an exhaust gas stream or in an industrial process. The conversion of pollutants such as hydrocarbons and carbon monoxide is done by using an oxidation catalyst that oxidises these pollutants mainly to carbon dioxide. Catalysts can be both heterogeneous and homogeneous i.e. in a different phase or in the same phase as the reaction media respectively. In this work heterogeneous catalysis will be discussed.

Heterogeneous catalysis has some advantages such as an easier separation from the reactants/products and longer life-time. The design of the catalyst depends on the application and its efficiency will depend much on its properties such as activity, surface area, pore diameter and deactivation sensitivity. These areas are discussed below.
Noble-Metal Catalysts
Noble-metal catalysts such as Pt or Au are the most common oxidation catalysts. This is due to their high selectivity to oxidation reactions. The main drawback with these noble-metal catalysts is the cost. This is why the interest of new catalysts that are not based on noble-metals is increasing. [6]

Non-Noble-Metal Catalysts
Non-Noble-metal catalysts are considered to be a low cost alternative to replace the noble-metal-catalysts. The challenge is to find a non-noble-metal that can compete with the noble-metal catalysts from an catalytic point of view. Regulations have made it even more important to make the catalysts more efficient and the acceptable amounts of pollutants in the exhaust gases are decreasing. This makes it hard to find a non-noble-metal catalyst since they are not as effective as the noble-metal-catalysts. [7] Research has shown that there are non-noble-metal catalysts that have good potential when it comes to the reduction of CO such as the CuO/CeO$_2$ catalyst. But the disadvantage with these catalysts are the short lifetime caused by other compounds in exhaust gases that can cause poisoning of the catalyst. Hence further research and development of these catalyst are required.

Catalytic Reaction  The catalyst decreases the energy required for a reaction to take place. A catalytic reaction is shown in a energy diagram in figure 3a and compared with the energy required without the catalyst. The surface reaction on the catalyst have the main reaction steps of adsorption of the specie, catalytic surface reaction followed by desorption of the products. Figure 3b shows the main steps in a heterogeneous catalytic surface reaction.

Figure 3: Catalytic reactions.
3.1 Catalytic Activity

Transition metals have different abilities to catalyze reactions, so do the corresponding oxides, sulfides, carbides and nitrides of these metals. This is due to their many different surface electronic states of low energy that makes the metal catalyst able to easily break or make bonds at the catalytic surface. Different metal states are active depending on the reaction that the catalyst is supposed to catalyze, for example metal oxides are used in oxidation reactions and sulfides for hydrodesulphurization reactions. Other reaction parameters may also have influence on the catalytic activity such as temperature or pressure; the impact can mean an increase as well as a decrease in catalytic activity. Depending on the metal that is used and for what kind of reaction it is intended to catalyze. [9]

3.2 Catalyst Support

The catalyst support is the material where the active catalyst is coated onto. There are some different shapes and forms of catalyst support and the most common are pellet and monolith.

Pellet

The first catalytic converters introduced in the 1970s consisted of pellets. These pellets particles are about 2.5-5 mm diameter coated with catalytic material and placed in a steel container which is the catalytic converter. The pellets are usually made of gamma-alumina. The main disadvantage with the pellet catalytic converter is the large pressure drop and hence the other alternative monolith is a better option from this point of view. Figure 4 shows a catalytic converter containing a bed of pellets. [10]

Monolith

Today catalytic converters made of monolith is standard for catalyst control such as automotive and diesel applications. The monolithic substrate consist of a honeycomb structure made of either ceramics or metal. The substrate contain several channels where the catalytic material is coated on the walls in a thin layer inside each cell. The main advantage of the monolith substrate compared to pellets is the low pressure drop. The most common monolithic catalyst substrate for diesel engines have a cell density of 300-400 cpsi and for gasoline engines 400 cpsi. Figure 5 shows a catalytic converter containing a monolith substrate. [10]
3.3 Catalytic Selectivity

The catalytic selectivity is an important parameter when it comes to catalyst properties. It refers to the amount of a produced product relative to other products [9]. The catalytic selectivity, for a CO oxidation reaction can be calculated with equation 1 [12].

\[
S_{CO} = \frac{0.5 \cdot (\lbrack CO \rbrack_{in} - \lbrack CO \rbrack_{out})}{\lbrack O_2 \rbrack_{in} - \lbrack O_2 \rbrack_{out}} \times 100\% \tag{1}
\]

3.4 Carrier material

Characteristics for a good catalytic carrier are high porosity, high surface area, large pore volume and have a possibility to remain its catalytic phases stable during catalytic reactions. Typical properties for commonly used carriers are surface areas of 1-1500 m\(^2\)/g (BET area), pore volumes of 0.4-1.14 cm\(^3\)/g and pore diameters of 0.6-2200 nm for different catalytic carriers. A common way to measure the surface area of a catalyst is BET analysis (Brunauer-Emmet-Teller).

3.5 Catalyst Deactivation

Catalyst deactivation means that the catalytic activity of a catalyst is reduced. The design of a catalyst for a catalytic process so that it is resistant against deactivation is one of the greatest challenges. Definition of a catalyst is that it accelerates the reaction rate of a reaction without being consumed itself i.e. it should work forever. But this is not the case; the catalyst will not work forever because of other compounds present or other phenomenon. A catalyst can be deactivated by poisoning, fouling, coking and carbon deposition or by thermal degradation and sintering, some deactivation processes are reversible while some are not. [9]

3.5.1 Poisoning

The principle of catalyst poisoning is that a compound, not involved in the catalytic reaction, adsorb onto the catalytic sites and blocking the reactants from the active sites. Characterizing the poison itself it needs to have a larger adsorption strength compared to the other species (reactants). In other words, the poison is competing against the reactants for the active sites. Different reactions are sensitive to different compounds. Some common poisons are hydrocarbons, sulfur compounds, ammonia, water and carbonyl sulfide (COS). Different poisons are more poisonous to specific metals than other. The mechanism of catalyst poisoning is illustrated in figure 6. [9]
3.5.2 Fouling, Coking and Carbon Deposition

Deactivation caused by fouling is because of physical deposition of compounds onto the catalytic surface resulting in blockage of active sites and/or pores. It could also include deposition of carbon and coke in porous catalysts. The function of the fouling and carbon deposition is blockage of the active sites and clogging of the catalyst pores, resulting in deactivation of the catalyst. The mechanism of fouling/coking is illustrated in figure 7.

3.5.3 Thermal Degradation and Sintering

Sintering refers to deactivation or loss of active surfaces by changes in catalyst structure. Two typical sintering processes are crystallite growth in catalytic phase, which leads to loss of catalytic surface area, and pore collapse on metal crystallites leading to loss of support area. Water vapor usually accelerates the sintering process that takes place at around 500°C. An example of thermal degradation is chemical formation of volatile compounds. The effect on catalytic activity depends on if the reaction that takes place is structure sensitive. This means that the reaction may be dependent on metal crystallite size changes. For a reaction that is not structure sensitive the sintering process has no or very low effect on the catalytic activity. [9] The mechanism of sintering is illustrated in figure 8.
3.6 Prevention of Deactivation

The life-time of a catalyst may vary from seconds to several years. An effective catalyst and its life-time can have a large impact on the economics for an industrial process. Catalytic deactivation can not be avoided but the rate of catalyst deactivation can be regulated through control of for example; reaction parameters, catalyst properties and feedstock composition. Prevention methods for the different deactivation mechanisms presented previously are discussed below. [9]

Poisoning

To prevent catalyst poisoning the most effective way is to change the composition of the feed gas, i.e. reduce the concentrations of impurities. This is due the irreversibility of the catalyst poisoning mechanism. Alternatively the catalyst can be designed in a way so that it can be more resistant against poisoning. One example when designing a catalyst to prevent poisoning is to add ZnO which forms ZnS, for a sulfur sensitive catalyst. [13]

Coking

By optimizing the catalyst design and process parameters the coke deposition may be controlled. Critical for the coking process is the equilibrium between coke production and coke removal. The coke on the surface can be removed by $H_2$, $H_2O$ or $O_2$ in forms of $CH_4$, $CO$ or $CO_x$. If equilibrium is not reached, i.e. the coke formation has a higher rate than the coke removal, the coke deposition will be large and a regeneration process is required. Process parameters that can affect the coking process are for example pressure, temperature and flow rate of gas/liquid over the catalyst. [14]

Sintering

Temperature is the most important parameter for the sintering process due to the fact that metal crystallite growth is a thermally activated process. Most sintering processes are irreversible so by keeping the operation temperature low, sintering can be reduced. Usually temperatures 0.3-0.5 times the melting point of the metal reduces the rate of sintering to a minimum level. Metal crystallization and structural changes are also accelerated by water vapour. So by lowering the operation temperature and minimize water vapour concentration the sintering process can be minimized. [9]

3.7 CO Oxidation Catalysts

For a oxidation catalyst to be a good CO oxidation catalyst it needs a good adsorption possibility. Compounds that are well studied and known to be good CO oxidation catalysts are Pt, Rh, Pd, Ir, Ru, Cu and Au. The metal catalyst that works as the CO oxidation material have a better possibility for adsorption of the carbon monoxide if it has the ability to form a positive charge, for example $Cu^+$. This makes the carbon monoxide adsorption to the surface faster. [15]
3.7.1 Ceria-Supported Catalyst - Ce/O

The most important property for the carrier material is the oxygen storage property. Ceria is used in automotive catalysts specifically for its good oxygen storage properties. This means that the ceria oxide can provide oxygen for the oxidation reaction when the concentration of oxygen in the air is not high enough i.e. the pressure of oxygen in the gas phase decreases below the stoichiometric value. [15]

4 Analysis Instruments/Characterization

4.1 Gas-Chromatography - GC

Gas chromatography (GC) is a separation technique that is used to separate and analyse compounds in a gas stream, for example CO, hydrocarbons and CO$_2$, but not water. The GC consists of an injection port where the sample is injected, a column, carrier gas control equipment, a heating source that controls the temperature of the injection port and column, usually ovens and heaters, and a detector that reads the results from the column. After sample injection a carrier gas which is an insert gas carry the molecules from the analyte stream through the GC column, where the different molecules are measured. Common carrier gases are helium, nitrogen and argon. Each molecule have a specific retention time in the column which means they will exit the column at different time. By calibration of the GC you can find out the retention time of specific compounds or molecules. The results from a GC is shown in a graph where you get different peaks at different points during the run, where each peak represent a molecule. From the calibration you can integrate an area under that peak and quantify the compound. [16]

4.2 Scanning Electron Microscopy - SEM

This technique uses a beam of electron that generates signals at the surface of the solid sample. From this different information such as morphology, composition (chemical) and crystalline structure can be derived. With SEM pictures of the surface can be achieved with a magnification up to 100,000 times which can be useful when you want to compare the structure of different samples and find different compounds present on the surface. [17]

4.3 X-Ray Diffraction - XRD

XRD applies X-ray beams onto a powder sample to characterize the structure of the crystals. By alternating the incoming angle $\alpha$ of the beam the atoms will diffract the beam in different angles. The collected data results in a diagram from which the crystalline structure of the sample can be evaluated. [18]

4.4 Brunauer-Emmet-Teller - BET

BET is a analysis method that is used to characterize the surface area of a substance. By measuring the amount of a gas that is adsorbed to the surface you can decide the total surface area of the substance you desire to measure. Usually nitrogen gas is used as adsorbent and the amount of adsorbed nitrogen can be measured by volumetric or
continuous flow. [19] These measurements were done in the previous thesis and will not be repeated, a brief discussion about the results are done in the discussion part.

5 Experiments

5.1 Catalyst Preparation

There are two common preparation methods of catalyst coating material in laboratory scale, the incipient wetness impregnation and co-precipitation methods. These two methods were used in the previous works for catalyst preparation and are briefly described below.

5.1.1 Incipient Wetness Impregnation

With this method the active material is dissolved in a solution and then mixed with the supporting material and disperse into the pores. The support $\text{CeO}_2$ was prepared by calcination of the Ce-nitrate precursor in a oven at 500 $^\circ$C for 5 hours. During this process the $\text{CeO}_2$ structure is generated. The total pore volume of the $\text{CeO}_2$ was determined by BET analysis and from this the correct amount of active material to saturate the pores could be calculated. This was done until the active material solution was completely impregnated onto the supporting material pores. Finally the wash coat was dried in a oven at 110 $^\circ$C over night. This preparation method was used in previous work by [20]. The incipient wetness impregnation method was used only for preparation of the Pt catalysts.

5.1.2 Co-precipitation

The metal precursors for the coating material were dissolved in deionized water together with the active material of the catalyst. For pH control in the mixture sodium carbonate was used with a concentration of 1 M. For precipitation the solutions were dropped into a flask with continuous stirring with pH kept between 8-10. After complete mixing of the solutions the mixtures were aged during continuous stirring for 3 hours, this was done to make sure to complete any further reactions. The samples were then filtered and washed with distilled water to remove any ions and then dried in a oven at 110 $^\circ$C over night. After the drying the powder was grinded and calcined at 500 $^\circ$C for 5 hours, this is done to remove any volatile compounds left in the material. Preparation of catalysts were done in 2014 by [20].
5.1.3 Prepared Catalysts

Different catalysts were prepared in previous works with different active materials. The catalysts that were used in this project are presented in table 1, together with their preparation methods and compositions.

Table 1: The different catalysts that are used in the experiments. Co-P: Co-Precipitation method, IWI: Incipient Wetness Impregnation, CPSI: cells per square inch

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Active material</th>
<th>wt-% on supporting material</th>
<th>Preparation method</th>
<th>CPSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MnO/CeO₂</td>
<td>7</td>
<td>Co-P</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>CuO/CeO₂</td>
<td>7</td>
<td>Co-P</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>CuO/CeO₂</td>
<td>14</td>
<td>Co-P</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>CuO/CeO₂</td>
<td>14</td>
<td>Co-P</td>
<td>600</td>
</tr>
<tr>
<td>5</td>
<td>Pt/CeO₂</td>
<td>7</td>
<td>IWI</td>
<td>400</td>
</tr>
</tbody>
</table>
5.2 SET-UP

The set-up that is used to analyse the exhaust gas is shown schematically in figure 9.

![Diagram of the complete system excluding the micro-GC.](image)

**Figure 9:** Schematic figure of the complete system excluding the micro-GC.

The sampling from the exhaust gas pipe is sucked through the system by a pump that is placed at the end. Before the pump there is a filter that removes the remaining water from the gas and a small fraction is sucked into the micro-GC. Before this filter there are three main water removal steps. The first step after the sampling is a beaker which is used to decrease the temperature of the gas. This is followed by a condenser that uses cooling water to condensate as much water as possible. Finally there is a column containing phosphorous pentoxide, which is a strong desiccant. The desiccant gets coloured depending of the amount of water it has absorbed, this helps you to know when the desiccant is saturated with water and needs to be replaced with fresh desiccant. Figure 10 shows the water removal system. Two pipes was connected to the exhaust gas pipe, one before and one after the catalyst which made it possible to easily switch when measuring the gas before and after the catalyst. Previously the catalyst was placed inside the reactor, but during this work the catalyst was placed in the exhaust gas pipe, as shown in figure 1.
Figure 10: Water separation system before the sample enters the micro-GC. 1: Sample from exhaust gas pipe. 2: Beaker for temperature drop. 3: Condenser column to remove water vapor by the use of cooling water. 4: Phosphorus pentoxide column which absorb the water that is left. 5: Final filter that removes any particles and impurities.

Figure 11 shows the micro-GC that was used for analysis of the exhaust gas.

Figure 11: Micro-GC for analysis of the exhaust gases. The micro-GC is connected to a laptop where the software is controlled.
Figure 12: The ReformTech heater system. Where: 1:Glycol for cooling. 2:Heater containing combustion chamber, fuel injection etc. 3:Exhaust gas pipe. 4:Sampling probe. 5:Catalyst holder containing the monolithic catalyst.

Figure 13: Thermocouples were used to measure the temperature after the heater. The temperature was measured before the catalyst, inside the catalyst and after the catalyst, representing no 1, 2 and 3 in the figure respectively.
5.3 Catalytic Activation Test

The activity of the catalyst were tested by running a ReformTech heater with different catalysts and measuring the concentration of CO in the exhaust gas. Since the exhaust gas contains some amount of water vapour (7-10 %) removal of water was necessary to avoid damage on the GC. This was done by a system containing a baker for temperature drop, a condenser to condensate out the water with circulating cooling water and a last water separation column containing phosphorus pentoxide. The last column containing phosphorus pentoxide was the most critical step of the water removal. This is since it is a very strong decissant and is supposed to remove the last part of water vapour remaining in the gas. The reason why not the decissant was the only water removal step is that it would be saturated with water very quickly and therefore some separations are used to remove the majority of the water before the phosphorus pentoxide column.

The exhaust gas before the catalyst was analysed for 90 minutes of run time. This was done to evaluate if the composition differs with time. The concentrations of the main components were stabilized after 30 minutes, as seen in figure 14. This test was done twice with the same results and the concentrations was ±0.6% after each 10 minutes of run time. The high values in the beginning is caused by the cold start where large amounts of CO is produced. The steady state temperature inside the catalyst was 420°C.

![Figure 14: Analysis of the exhaust gas before the catalyst. Temperature inside the catalyst 420°C](image)

The exhaust gas was also analyzed after the commercial catalyst that is used in the ReformTech heater. This was done as a reference. The concentration of CO was reduced to about 20 ppm as seen in figure 15. There are also high concentrations after the catalyst in the beginning of the run, this is caused by the high levels of CO that is produced during the start up of the system.
The test with the commercial catalyst were done to verify that the analysis method is solid and measures the desired compounds. Measurements of the exhaust gas before the catalyst has been done by ReformTech and are represented in table 2. These concentrations match the results in figure 14.

Table 2: Measurements of the exhaust gas before the catalyst.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration [% ppm for CO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>8,3-9,7</td>
</tr>
<tr>
<td>O₂</td>
<td>6,1-7,2</td>
</tr>
<tr>
<td>N₂</td>
<td>74,3-75,9</td>
</tr>
<tr>
<td>CO</td>
<td>300-750</td>
</tr>
</tbody>
</table>

During all test the parameters that could be affected were kept constant, these values are presented below:

- Lambda (\(\lambda\)), 1.45. This is a optimum value that also has been confirmed to be where the heater is working at its best condition, from a emission and efficiency point of view.

- Temperature, 410-420 °C inside the catalyst, was measured with a thermocouple inside the catalyst. It was shown that the small variance of 10 °C did not affect the emissions, but larger changes did.

- Sample flow to the micro-GC, 30 ml/min. This was automatically controlled by the micro-GC.
5.4 Deactivation Test

When testing the catalysts sensitivity against sulfur poisoning di-tert-butyl disulfide was mixed in the diesel so that a sulfur concentration of 300 ppm was reached. Sulfur is added to the fuel because the limitations of fuel content are different from country to country. A sulfur concentration of 300 ppm could occur if the catalyst is used in countries such as China or Russia. The concentrations before the catalyst were analysed when the diesel contained the sulfur and it did not affect the composition of the exhaust gas.

5.5 SEM analysis

The SEM analysis were done by a certified controller at KTH Kista. Small powder samples were collected from the catalysts, both fresh and used catalysts were analysed.

6 Result and Discussion

6.1 CO Reduction

Catalyst 1

Catalyst 1 with 7% MnO/\(\text{CeO}_2\) as the active material did not show any activity against carbon monoxide reduction. The measurements before and after the catalyst is shown in figure 16.

![Figure 16: Experiments with catalyst 1, MnO/\(\text{CeO}_2\) as active material. Temperature inside catalyst: 410 – 414°C](image)

It was also confirmed in previous work that the MnO/\(\text{CeO}_2\) catalyst was not active against the reduction of carbon monoxide. Since the catalyst did not show any activity the deactivation test with sulfur in the fuel were not tested.
Catalyst 2

Catalyst 2 with 7% CuO/\textit{CeO}_2 as the active material and 400 cpsi showed activity against carbon monoxide reduction. As seen in figure 17 the carbon monoxide concentration was reduced to 200-300 ppm after the catalyst. The reason why concentration was not reduced more could be a case of lack of active sites, which could be improved by increasing the surface area of the catalyst. For example a monolith with 600 cpsi could have given lower concentrations of carbon monoxide.

![Figure 17: Experiments with catalyst 2, CuO/\textit{CeO}_2 as the active material. Temperature inside catalyst: 420 – 423°C](image)

The concentration of carbon monoxide needs to be reduced to at least 20 ppm for the catalyst to be interesting and referred to as an effective catalyst.

Catalyst 3

Catalyst 3 with 14% CuO/\textit{CeO}_2 as the active material with 14 wt-% and the monolith with 400 cpsi. It showed similar activity for carbon monoxide reduction as catalyst 2. It reduced the concentration of carbon monoxide below 200 ppm and was kept constant at this level for 950 minutes. Sulfur deactivation tests were done with this catalyst and as seen in figure 18 the carbon monoxide concentration increased immediately when the sulfur fuel was used.
Figure 18: Experiments with catalyst 3, CuO/CeO$_2$ as the active material. The area between the black lines represent the runs where the diesel contains 300 ppm sulfur. Temperature inside the catalyst: 418 – 421°C

The catalyst was first tested with sulfur free diesel and reduced the CO concentration but not to acceptable levels. After the runs with sulfur added to the fuel it showed that the catalyst was completely deactivated. This deactivation is most likely caused by the sulfur present in the fuel.

Catalyst 4

Catalyst 4 has the same coating material as catalyst 3 but the difference is that catalyst 4 uses a monolith with 600 cpsi. This gives a larger catalyst surface and results in more reduction of carbon monoxide. As seen in figure 19 in appendix catalyst 4 shows prominent activity and reduces the carbon monoxide concentration below the detection limit of the micro-GC (detection limit 5-10 ppm). The reduction of carbon monoxide was constant for about 640 minutes, at this point sulfur was added to the fuel. As seen in figure 19 the carbon monoxide concentration increases when the sulfur is added to the fuel. This increased concentration of carbon monoxide is most likely a result of the sulfur that is present in the fuel. This means that sulfur atoms or sulfur compounds functions as poisons, are occupying the active sites of the catalyst. This means that the carbon monoxide molecules are unable to bond to the catalytic surface and react and more and more carbon monoxide pass by over the surface without even interact with the catalyst. Eventually the majority or all of the active sites are occupied by the sulfur poisons and makes it impossible for the carbon monoxide to react on the catalytic surface and instead it just passes by and leaves the catalyst unreacted.
Figure 19: Experiments with catalyst 4, CuO/CeO$_2$ as the active material and monolith with 600 cpsi. The black line represent where sulfur is added to the fuel. Temperature inside the catalyst: 415 – 420$^\circ$C

Due to time limitations during this run it was not possible to test the catalyst with sulfur free diesel after being exposed of sulfur. But since it is the same coating material it is most likely to be the same case as the test with catalyst 3 where it was completely deactivated by the sulfur in the fuel.

**Catalyst 5**

Catalyst 5 has Pt as the active material. This test was done to compare the noble metals sensitivity against sulfur deactivation. As seen in figure 20 in appendix the Pt catalyst reduces the carbon monoxide to 50 ppm. The black line represent where the fuel contains 300 ppm sulfur and there is a small increase in carbon monoxide concentration but the catalyst is not completely deactivated.
Compared to catalyst 2-4 catalyst 5 did not deactivate completely. Though a small deactivation can be seen since the reduction of carbon monoxide does not go back to the levels where it was before the exposure of sulfur.

When comparing with previous work the main different in the tests is the difference in temperature. In previous work the temperature inside the catalyst was about 250°C. One important factor when it comes to the non-noble metal catalysts is the temperature dependency. It has been discussed in previous works that a higher temperatures makes a non-noble metal catalyst more efficient. If the results in this work are to be compared with previous work the conversion of carbon monoxide is considerably higher. This is most likely because of the higher temperatures that are achieved inside the catalyst in this work, which are about 410 – 420°C.

### 6.1.1 Pressure Drop in Fuel Filter

During the work there were some errors with the heater and it was working under different conditions from time to time. It was showed that the fuel filter before the heater was clogged which resulted in a small pressure drop through the fuel filter. This gave a lower temperature in the catalyst and the concentration of carbon monoxide rapidly increased. Figures 21 and 22 shows how the concentration of carbon monoxide increased during the runs. During these runs the temperature inside the temperature was 260 – 300°C, which means a decrease of about 150°C.
Figure 21: Test with catalyst 2, CuO/CeO$_2$ with pressure drop through the fuel filter. Carbon monoxide concentration after the catalyst.

Figure 22: Test with catalyst 2, CuO/CeO$_2$ with pressure drop through the fuel filter. Carbon monoxide concentration after the catalyst.

It can be discussed if the carbon concentration increase is caused by incomplete combustion of the fuel caused by the lower fuel pressure. This could give small droplets or an uneven spray of the fuel. The other reason for the increase in carbon monoxide could be the lower temperature in the catalyst. These runs were not considered to be reliable results for the analysis of the catalytic activity of the catalysts, but they show an interesting trend how the carbon monoxide concentration depends on the temperature and/or the fuel pressure. Further tests where these parameters are controlled need to be done to show how they correlate with the carbon monoxide concentration.

6.2 SEM Analysis

SEM analysis were done on catalyst 2, 3 and 5. Due to time limitations all catalysts were not analysed with SEM. All results from the SEM analysis are presented in the appendix.

Catalyst 2, 7%CuO/CeO$_2$

Figures 23-26 shows the SEM results for catalyst 2. Figure 23 shows the CuO/CeO$_2$ catalyst not exposed to sulfur and figure 24 shows the catalyst after being exposed
to sulfur. It cannot be shown from these figures that sulfur is present on the surface, but it can be proven from the spectrum that sulfur actually is present on the catalyst that has been exposed to sulfur. As seen in figure 26 sulfur was detected compared to figure 25 which represent the catalyst not exposed to sulfur.

Figure 23: Catalyst 2 not exposed to sulfur.

Figure 24: Catalyst 2 after being exposed to sulfur.
Catalyst 3, 14%CuO/CeO₂

Figures 27-30 in appendix shows the SEM results for catalyst 3. As expected copper is detected in both figure 28 and 30 but no sulfur is detected in this case as seen in figure 30. This could be since the SEM analysis is very sensitive to where you choose to take the pictures and analyse the sample. Sulfur is expected to be present in figure 30 but it is not and this is probably due to the human error. If there was more time for the SEM analysis more analysis of the same sample could have been done and possibly give different results and show that sulfur is present. From the figures 27-30 it cannot be proven that the sulfur is present in the sample but considering the deactivation shown in previous experiments it is most likely that it is caused by sulfur.

Catalyst 5, 7%Pt/CeO₂

Figures 31-34 in the appendix shows the SEM results for catalyst 5. Platina is only detected in figure 32 and not in figure 34. The difference between the spectrum is that sulfur is detected in figure 34 which is expected. Catalyst 5 was slightly deactivated as shown in the previous experiments and the sulfur that is present is probably the reason of deactivation and the decrease in activity that was shown in the analysis with the micro-GC.
7 Conclusion

Previous work were focusing on finding a catalyst based on a non-noble metal that showed activity against carbon monoxide oxidation. It was concluded that the CuO/CeO$_2$ catalyst showed prominent properties to work as a oxidation catalyst but it was only tested for shorter times. Since a catalyst is supposed to work for a long time it is hard to get results that can be compared to a commercially used catalyst but it has been showed that the copper catalyst has the ability to work as well as today’s commercial catalysts for a shorter time. The copper coatings that were used in this project had the correct properties and from the results the decisive parameter is the available catalytic surface area.

The catalyst that showed the best carbon monoxide oxidation capacity was catalyst 4 with 14 wt-% CuO/CeO$_2$ on a monolith with 600 cspi. Previous reports where the amount of active material in the coating was increased did not show any improvement. The amount of CuO/CeO$_2$ was tested at a maximum of 28 wt-%, there might be a optimal amount of active material between 14 and 28 wt- % where the catalytic surface area is not as important or possibly could be decreased.

It was proven that all non-noble catalysts used in this project were sensitive to sulfur poisoning. This is due to the blockage of active sites caused by the sulfur poisons. Most likely additives needs to be added to the coating material to avoid deactivation caused by sulfur. The problem with additives is that it may affect the catalysts oxidation properties and decrease the activity. More research and experiments needs to be done to find a catalyst based on non-noble metals that is resistant to sulfur poisoning and yet have prominent oxidation properties. One issue with the sulfur deactivation tests was that the concentration of sulfur may have been to high which gave a very fast deactivation. The deactivation tests could have been done with different concentrations of sulfur in the fuel, and not only one high concentration.

The preparation methods for the catalyst is a critical point since the method determines important catalytic properties such as surface area and pore volume. Two different persons prepared catalyst 1-2 and 3-4 and the methods were the same but may have been executed with some differences. This can cause some differences in catalytic properties and from the SEM results it is hard to compare the differences in morphology and determine what the true differences are between the catalysts.

The main difference in this work compared to previous work is that the outlet exhaust gas temperature from the heater is higher, which gave a increase of temperature inside the catalyst. Since the same catalysts were used in this project and more reduction of carbon monoxide was achieved it shows that the temperature has a major impact on the efficiency of the non noble metal catalysts.

It can be the concluded that the copper catalyst is a good non-noble metal oxidation catalyst for oxidation of carbon monoxide. But the drawback with this catalyst is its sensitivity against sulfur poisoning which is a critical part when it comes to commercialize the catalyst. Even tough the long time runs showed that there is no deactivation caused by sintering, coking or another deactivation phenomenon of the
non-noble metal catalyst.

8 Future Work

- Use different wt-% of CuO/CeO$_2$ in the coating to find a optimum amount of active material.

- The use of additives that prevent sulfur deactivation should be investigated and experimented with.

- Find other non-noble metals than copper that could have the same activity against carbon monoxide oxidaiton but may not be as sensitive against sulfur poisoning.

- Perform the deactivation tests in a different way. The concentrations of sulfur could gradually be increased, for example from 10 ppm and up to 300 ppm.
References


9 Appendix

SEM Analysis

Figure 27: Catalyst 3 not exposed to sulfur.

Figure 28: Spectrum of detected compounds in the sample with catalyst 3 not exposed to sulfur.
Figure 29: Catalyst 3 after being exposed to sulfur.

Figure 30: Spectrum of catalyst 3 after being exposed to sulfur.
Figure 31: Catalyst 5 not exposed to sulfur.

Figure 32: Spectrum of detected compounds in the sample with catalyst 5 not exposed to sulfur.
Figure 33: Catalyst 5 after being exposed to sulfur.

Figure 34: Spectrum of catalyst 5 after being exposed to sulfur.
Catalysts

Figure 35: Previously prepared catalysts. 1-3: Copper catalysts. 4-6: Cobalt catalysts (not tested in this work). 7-12: Manganese catalysts