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Oxidation Catalysts in Exhaust Aftertreatment Systems for Green-Methanol Engines

Bench Testing and Emission Control Analysis

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Oxidation Catalysts in Exhaust Aftertreatment
Systems for Green-Methanol Engines
Investigating Methanol Oxidation Catalysts for Green-Methanol Engines: Bench Testing and Emission Control Analysis
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Abstract

This thesis investigates methanol oxidation catalyst (MOC) coatings for reducing emissions from marine methanol engines. Three different catalysts were synthesized with Pt-loadings of 1.5, 1.0, and 0.5 wt% on Al_2O_3 support. The oxidation activity of the catalysts was tested using a syngas bench test, where the impact of different NO_x feeds on methanol conversion and formaldehyde formation was investigated. The result showed that NO_x highly impacts the oxidation activity for all of the catalysts at low temperature, since the temperature limit of 100°C for full conversion of methanol is increased to 200°C in presence of NO_x. A decrease in oxidation activity in presence of NO_x was especially seen when only NO was fed, while NO_2, being a strong oxidizing agent, increased the methanol conversion in comparison to NO. Additionally, the methanol conversion showed a dependence on temperature and loading, where low temperature and loading resulted in a decreased methanol conversion. The presence of NO_2 additionally increased the formation of formaldehyde and caused deactivation of the catalysts. This was especially seen at 120°C, where increased levels of formaldehyde, coupled with less active catalysts, resulted in prolonged recovery times. A correlation between formaldehyde formation and temperature was also seen, where lower temperatures significantly increased the formation. However, the catalyst loading had a minor impact. For 1.5 and 1.0 wt% Pt loading, the results were comparable, while a small increase in formaldehyde formation was seen for 0.5 wt% Pt loading at 200°C. The result also showed that at high temperature and loading, there was a significant increase in the NO_2/NO_x ratio, accompanied by increased concentrations of an unidentified N-species. These findings present valuable insights into the performance of MOC coatings, highlighting the significant impact of NO_x on methanol oxidation activity and formaldehyde formation, and suggest ways for optimizing catalyst formulations to reduce emissions from marine engines.

Keywords: methanol, oxidation catalyst, syngas bench test, platinum, catalyst loading, emission, formaldehyde, NO_x

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

DF	Dual-fuel
DOC	Diesel Oxidation Catalyst
EEA	European Energy Agency
HFO	Heavy Fuel Oils
IMO	International Maritime Organization
LHV	Lower Heating Value
LNG	Liquified Natural Gas
LOT	Light-off Temperature
MOC	Methanol Oxidation Catalyst
OC	Oxidation Catalyst
PGM	Platinum Group Metals
PM	Particulate Matter
SCR	Selective Catalytic Reduction
VOC	Volatile Organic Compounds

Contents

1. Introduction

1.1 Background

The transport sector is a crucial artery for the global movement of goods and people, serving as the backbone of interconnected economies and societies. Maritime transportation accounts for 90% of global trade, a figure that continues to climb annually [1]. However, this mode of transport also poses significant environmental challenges. A study conducted by the European Energy Agency (EEA) in 2019 revealed the significant environmental impact of maritime transport, attributing 20.98% of global nitrogen oxide (NO_x) emissions, 11.80% of sulphur oxide (SO_x) emissions, 8.57% of particulate matter (PM) 2.5 emissions, 4.63% of PM10 emissions, and 1.94% of carbon monoxide (CO) emissions to this sector. One frequently used fuel in marine engines is diesel, due to it being both an efficient and reliable fuel [2].

Diesel fuel consists of a blend of complex, heavy molecules, including aromatics and several unsaturated compounds, which contributes to the formation of harmful exhaust emissions such as CO, hydrocarbons (HCs), and NO_x [2]. Moreover, since the C/H ratio of diesel is low, there is a high tendency for the formation of smoke precursors. Unburned carbon atoms are also likely to occur in diesel fuel and due to the complex structure of diesel, the structure of unburned and partially oxidized HCs are complex and extend over a large range of molecular sizes, leading to increased smoke emissions.

One way of decreasing maritime emissions is through alternative fuels such as methanol, ethanol, ethane, and liquefied natural gas (LNG) [3]. Methanol and LNG are the fuels with the highest potential in the maritime sector due to their robust supply infrastructure and the availability of biofuel counterparts. Methanol is of special interest since space and modification requirements on ships are moderate, and if optimum combustion conditions are provided, methanol fuel increases engine efficiency.

In contrast to conventional diesel fuel, methanol has a lower molecular weight, simpler molecular structure, higher oxygen contents, and lower sulfur and aromatic contents [2]. As a consequence, methanol moderately reduces CO_2 emissions and highly decreases NO_x, SO_x, and PM emissions [3]. Methanol has a high H/C ratio and since it is not a long-chain hydrocarbon, methanol does not form PMs to the same extent as diesel. Additionally, the unburned and partially oxidized HCs are in a smaller size range and less complex than those formed by diesel fuel [2, 3]. The formation of SO_x is also reduced due to the sulfur-free structure.

Although the formation of harmful gases are decreased with the use of methanol instead of diesel for marine engines, a transition to methanol requires the development of a new methanol oxidation catalyst (MOC). The MOC needs to be specified for the reduction of harmful gases caused by methanol combustion, including the conversion

of unburned methanol, HCs, CO, and formaldehyde into harmless compounds.

1.2 Aim

The aim of this thesis is to verify different MOC coatings, and investigate their efficiency for reducing harmful emissions from marine methanol engines. This will be done by syngas bench testing three different catalysts with different loadings of Pt on Al_2O_3 support: 0.5 wt%, 1.0 wt%, and 1.5 wt%. The effect of NO and NO_2 on the oxidation of methanol and the formation of formaldehyde will also be studied by varying the feed concentrations of NO and NO_2 to the MOC.

2. Theory

2.1 Diesel oxidation catalyst

The diesel oxidation catalyst (DOC) is typically the first component following the engine and it is used to convert hazardous emissions into harmless products [4]. The DOC has been integrated into diesel exhaust systems since 1967, when regulations and limitations regarding harmful emissions from diesel engines were implemented. Diesel engines generate various harmful emissions from different reactions; incomplete combustion causes the formation of CO as well as unburned HCs and soot. Reactions involving other HCs can produce polynuclear aromatic components and various volatile organic compounds (VOCs), which can either be emitted directly or undergo further reactions with NO_x in sunlight. NO_x is formed from the nitrogen-containing air during combustion, and to a lesser extent, from nitrogen bound within the fuel. Although NO_x emissions are considered primary pollutants, they also undergo photochemical reactions, leading to the generation of ozone — a potent oxidizer, irritant, and component of smog.

2.1.1 Structure

The structure of a DOC is generally based on cordierite (ceramic) monoliths coated with washcoats containing a catalyst support and precious metals, and in some cases promoters and stabilizers [4]. The monolith is a catalyst support that is typically a solid, single, and continuous piece. It is characterized by its honeycomb-like structure with small (0.5 - 4 mm) parallel channels separated by catalytic walls [5]. Figure 2.1 illustrates the structure of the monolith along with the constituent parts of the catalyst. The cordierite composition gives the monolith unique properties which are crucial for successful catalysis. These include resistance to thermal shock due to a low thermal expansion coefficient, porosity, and a well-suited pore size distribution for easy washcoat application and robust adherence, adequate heat resistance with a melting point exceeding 1450°C, ample strength for survival in an automotive exhaust environment, and compatibility with washcoat and catalyst materials [6].

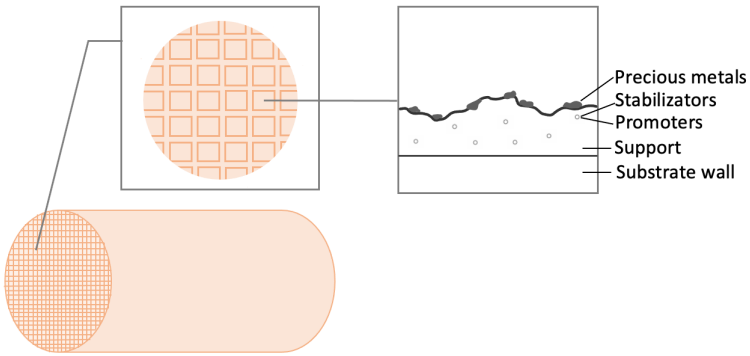

Figure 2.1: Monolith structure with the constituent parts of the catalyst.

2.1.1.1 Catalyst support

The washcoat contains a catalyst support with a high surface area, resulting in highly dispersed precious metal sites [4]. This increases the exposed surface area of the active component for reactions and reduces the necessary amount of precious metals. Consequently, this contributes to lowering the overall catalyst cost. Moreover, the characteristics of the catalyst support can impact performance by modifying the thermal stability of both the active component and the support, as well as influencing surface area, pore volume, and surface reactivity. Examples of washcoat materials are Al_2O_3, SiO_2, and zeolites, each with different properties that can be tailored for the target reactions.

2.1.1.2 Precious metals

The precious metal is the primary active site of the reaction in a catalyst. Platinum group metals (PGMs), specifically platinum (Pt) and palladium (Pd), are the most common precious metals used in DOCs, due to their good oxidation performance [4]. The metals may be used individually or in combination, depending on the desired oxidation characteristics. While both Pt and Pd serve as adsorption sites for oxygen and HCs, Pt is recognized for its stereotypically higher oxidation activity and lower relative surface oxidation coverage. In the oxidation of heavier weight HCs, Pt also outperforms Pd, however, at elevated temperatures, the activity of Pt decreases due to thermal degradation. Pd catalysts, which often form Pd oxides, have shown more resistance to sintering at high temperatures than Pt. However, catalytic oxidation activity of Pd can be decreased by other factors including Pd's susceptibility to sulfur, water inhibition/poisoning, trace lead, and phosphorous. In contrast to this, Pt exhibits good oxidation activity and maintains sufficient performance at lower temperatures, even in the presence of SO_2, a common catalyst poison. Although Pt can be poisoned by SO_2, it is more resistant to SO_2 poisoning compared to Pd.

The catalyst can also be composed of a bimetallic Pt/Pd combination [4]. This can give improved properties such as slower sintering than monometallic Pt-catalysts. While the exact structure of these Pt/Pd-catalysts remains uncertain, two perspectives offer insights into their configuration. The first is that the catalyst is an alloy of Pt and Pd, where the particles segregate to form distinct Pt and Pd crystallites between 300-700°C. The interaction between neighboring Pt and Pd crystallites is thought to restrict the mobility of the metal particles, which is hindering particle growth and maintaining dispersion. The second perspective suggests that Pt and Pd persist as separate entities, forming bimetallic structures that may segregate in oxidizing environments, forming bimetallic clusters consisting of a Pt core surrounded by an outer shell Pd. The bimetallic behavior is however difficult to predict.

2.1.2 CO oxidation

On a Pt-catalyst, CO adsorbs by the carbon bonding to Pt, while the oxygen faces away from the catalyst [4]. There have been some disagreements on the reaction

mechanism of CO oxidation on Pt-catalysts, but the currently accepted mechanism is the Langmuir-Hinshelwood dual-site mechanism, with the elementary steps shown in Reactions 2.1 - 2.5, where represents an active site on the catalyst surface [4, 7].

$$\mathrm{CO} + {}^{*} \rightleftharpoons \mathrm{CO}^{*} \tag{2.1}$$

$$\mathrm{O_2} + {}^{*} \longrightarrow \mathrm{O_2}^{*} \tag{2.2}$$

$$\mathrm{O_2}^{*} + {}^{*} \longrightarrow 2\,\mathrm{O}^{*} \tag{2.3}$$

$$\mathrm{O}^{*} + \mathrm{CO}^{*} \longrightarrow \mathrm{CO_2}^{*} + {}^{*} \tag{2.4}$$

$$\mathrm{CO_2}^{*} \longrightarrow \mathrm{CO_2} + {}^{*} \tag{2.5}$$

2.1.3 HC oxidation

Similar to CO, complete oxidation of HCs from the exhaust gas tends to follow the Langmuir-Hinshelwood dual-site mechanism, where O_2 and HCs adsorb to the Pt surface at different sites and the surface reaction is the rate determining step [4]. At temperatures below the light off-temperature (LOT), the adsorption of HCs is stronger than the oxygen adsorption, resulting in limited surface oxygen for the surface reaction between HCs and oxygen. There are many possible reactions and elementary steps for the oxidation of HC, depending on the structure of the HC. The adsorption mechanisms and a general possible surface reaction of HCs and O_2 are shown in Reactions 2.6 - 2.8 [4].

$$\mathrm{O_2} + {}^{*} \longrightarrow \mathrm{O_2}^{*} \longrightarrow 2\,\mathrm{O}^{*} \tag{2.6}$$

$$\mathrm{HC} + {}^{*} \rightleftharpoons \mathrm{HC}^{*} \tag{2.7}$$

$$\mathrm{HC}^{*} + \mathrm{O}^{*} \longrightarrow \mathrm{CO_2} + 2\,{}^{*} \tag{2.8}$$

2.1.4 NO oxidation

While the primary function of the DOC is to oxidize HCs and CO, the oxidation of NO_x is a crucial step for the SCR process following the DOC [4]. The NO_x from diesel exhaust is composed of approximately 90% NO, which will be partially oxidized to NO_2. The oxidation of NO is kinetically controlled at low temperatures and thermodynamically controlled at higher temperatures. Moreover, the reduction of NO_2 to N_2 by CO or HCs is not energetically favored in the lean exhaust environment typical for diesel engines. Nonetheless, it has been observed that engine-out NO_2 can be reduced to NO by CO and/or HCs prior to NO oxidation in DOCs, resulting in a reduction in NO_2 concentration, which could negatively impact the SCR process.

The reaction mechanism for NO oxidation, proposed by Salman *et al.*, are outlined in Reactions 2.9 - 2.12 [8].

$$\mathrm{NO} + {}^* \rightleftharpoons \mathrm{NO}^* \tag{2.9}$$

$$\mathrm{O_2} + 2\,{}^* \rightleftharpoons 2\,\mathrm{O}^* \tag{2.10}$$

$$\mathrm{NO}^* + \mathrm{O}^* \rightleftharpoons \mathrm{NO_2}^* + {}^* \tag{2.11}$$

$$\mathrm{NO_2}^* \longrightarrow \mathrm{NO_2} + {}^* \tag{2.12}$$

2.1.5 Deactivation

Catalyst deactivation is an inherent process observed in all catalysts [4]. It can be broadly categorized into two main types: selective and non-selective deactivation. Selective deactivation targets specific types of active sites, whereas non-selective deactivation affects all active sites uniformly. The reversibility of the deactivation depends on the exhaust conditions. Deactivation can occur through several different pathways, such as sintering of active sites, sulfur poisoning, and exposure to high temperatures. For instance, exposure to high temperatures may induce changes in the crystal morphology of the γ-alumina support, while sintering reduces the surface energy of the support. This decrease in surface energy results in decreased dispersion and pore blockage, leading to the encapsulation of precious metals. As a consequence, reactants are unable to access the active sites, thereby decreasing the overall catalyst activity. Sintering of precious metals can also occur, where the precious metals agglomerate, decreasing the dispersion.

2.1.6 Light-off temperature

The light-off temperature (LOT) is the temperature at which a catalytic converter gets activated and starts converting the emissions from the engine exhaust [9]. More specifically, the LOT is the inlet gas temperature at which 50% conversion is achieved [10]. At low temperatures, the efficiency of catalytic converters is highly decreased and larger amounts of harmful gases are emitted [9]. During the cold-start and warming period of an engine, the efficiency is close to zero. Two factors contributing to these high emissions at a cold-start are that the catalyst has not yet reached the LOT, and that most engines run with a rich mixture, meaning a high fuel to air ratio, during warm up.

When using a rich mixture during a cold-start, the supply of oxygen is not high enough for the oxidation reactions to begin [9]. Due to the incomplete combustion, harmful gases like unburned HCs and monoxides are released to the environment. For complete combustion to take place, the supply of oxygen needs to be increased and the catalyst must reach its LOT. The LOT for catalytic converters varies depending on the catalyst, exhaust and flow conditions, among other factors. Effective

conversion of exhaust gases for catalytic converters is normally between 250-300°C [9], but it can also be reached at significantly lower temperatures. For the conversion of NO using a Pt/Al_2O_3 catalyst, the LOT is reached already at 200°C under low temperature combustion conditions [11].

The LOT is mainly dependent on the chemical reaction kinetics over the catalyst, and is hence affected by the precious metal or washcoat system used for the catalysis. However, the high temperature conversion rate of gases like CO and HCs depends on the mass transfer conditions of the catalyst. The conversion efficiency can therefore be changed by altering the factors that determine the mass transfer coefficient or mass transfer area, such as substrate cell density and size of catalyst. The overall performance of a catalytic converter is hence dependent on both the catalyst technology and the substrate geometry [12].

2.2 Selective catalytic reduction

Selective catalytic reduction (SCR) systems are used in diesel engines to convert NO_x emissions into less harmful compounds, generally using urea ($CO(NH_2)_2$) as the reductant [13]. The SCR is typically placed after the DOC, where the DOC works as a gas pretreater by generating NO_2, enhancing the fast SCR reaction, but also by removing HCs from the engine exhaust, preventing potential HC interference with the SCR reactions. Using SCR systems for conversion of NO_x is advantageous due to its high efficiency and low cost. The most commonly used catalysts for SCR are vanadium-based oxides (VOx) supported by TiO_2, giving a conversion rate of over 90% at temperatures below 300°C [14]. However, at higher temperatures, VOx/TiO_2 catalysts are unstable and the activity decreases, requiring further development of Vanadium-based catalysts.

The general layout of a urea-SCR system for diesel engines is illustrated in Figure 2.2. Urea solution is pumped from an urea tank, upon which it is sprayed through an atomizing nozzle into the exhaust gas stream flowing into the SCR [13]. Before the gas stream enters the SCR, it passes through a static mixing device, which thoroughly mixes the exhaust gases and urea. When urea is mixed with the hot exhaust gas, it undergoes hydrolysis and thermal decomposition into ammonia. To further promote hydrolysis of urea, a hydrolysis catalyst is sometimes added before the SCR catalyst. After this, the ammonia and exhaust gas mixture enters the SCR catalyst, where NO_x is reduced to nitrogen. While SCR catalysts for land-based mobile applications usually uses coated substrates, homogeneous V_2O_5/TiO_2 extrusions are commonly used in marine engines. Finally, an ammonia oxidation catalyst is often added to the SCR system, in order to oxidize the ammonia slip, reducing the amount of ammonia emissions to the environment.

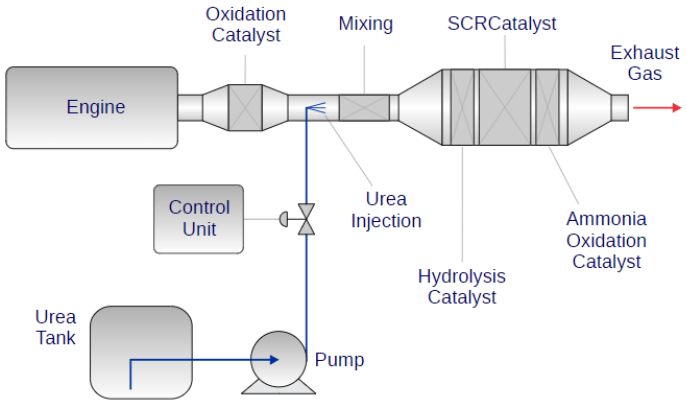

Figure 2.2: Urea-SCR system for diesel engines [13]

Following the decomposition of urea into ammonia, NO_x is reduced to elemental nitrogen and water according to Reaction 2.13-2.15 [15]. Reaction 2.13 represents the dominant standard SCR reaction, while Reaction 2.15 describes the fast SCR reaction.

$$4\,NO + 4\,NH_3 + O_2 \longrightarrow 4\,N_2 + 6\,H_2O \tag{2.13}$$

$$2\,NO_2 + 4\,NH_3 + O_2 \longrightarrow 3\,N_2 + 6\,H_2O \tag{2.14}$$

$$2\,NH_3 + NO_2 + NO \longrightarrow 2\,N_2 + 3\,H_2O \tag{2.15}$$

2.3 Methanol

Methanol (CH_3OH) is one of the most promising alternative fuels for maritime transportation as it reduces CO_2, NO_x, SO_x and PM emissions, while also increasing the engine efficiency [1]. Methanol can be produced from both fossil sources, including natural gas and coal, and renewable sources. Among the renewable sources is biomass, which includes wood, agricultural, and municipal waste, yielding biomethanol. Methanol can be also be produced from H_2 and CO_2, using renewable electricity and carbon capture from the atmosphere or from waste CO_2. This type of methanol is called electrofuel or e-methanol.

The use of methanol as a fuel for marine engines offers several advantages in comparison to diesel. As previously mentioned, methanol has a high H/C ratio, and since the HC chains are short, the combustion of methanol does not lead to the formation of PM [1]. The structure contains an oxygen atom, which promotes more efficient combustion with smaller air requirement, contributing to lower PM and CO_2 emissions, but also lower soot emissions. Since the methanol structure is sulphur-free, the combustion of methanol does not lead to the formation of SO_x. Additionally, methanol combustion in diesel engines can reduce the amount of polycyclic aromatic hydrocarbons formed, which is otherwise the main reason for diesel fuel toxicity. The

temperatures needed for methanol combustion is also lower than for diesel combustion, leading to less NO_x formation.

When using methanol instead of diesel as a fuel for marine engines, additional safety precautions are needed [1]. The International Maritime Organization (IMO) states that marine fuels should have flashpoints higher than 60°C, while methanol has a flashpoint of 12°C. In addition, methanol has invisible flames and relatively wide flammability limits. Although additional safety precautions must be taken, methanol vapor is heavier than air and methanol fire can be extinguished with water. Regarding storage of methanol in ships, methanol has physical properties that are similar to those of conventional marine fuels, such as heavy fuel oils (HFO), and can hence be stored in the same bunker with some minor modifications. Compared to diesel, methanol has a lower heating value (LHV) less than half the value of diesel, therefore, twice the tank volume of fuel is needed for traveling the same distance. However, since methanol is not as harmful as diesel if let out in the water, it can be stored in the double hull of the ship.

The use of methanol instead of diesel offers several advantages regarding the environment. Methanol is biodegradable and has a half-life time of 1-6 days in ground and water [1]. In water, methanol quickly dilutes and breaks down into CO_2 and water. The ecological threat of methanol spillage is hence significantly smaller, although it can cause increased sea vegetation. However, methanol is toxic for humans and can cause blindness if ingested, but can also be dangerous if it is absorbed through the skin or inhaled. Since methanol is odorless until 2000 ppm in air, the methanol fuel system on a ship must be completely closed to minimize potential risks. The main concerns regarding the application of methanol as a fuel is the difficulty of cold-start, warming up, low load operations, as well as formaldehyde emissions [2]. Emissions of formaldehyde are toxic for both humans and the environment. Exposure to formaldehyde may cause severe skin and eye irritation, but it has also been linked to an increased risk for different types of cancer, as well as negative reproductive effects. In addition, the breakdown of formaldehyde in the atmosphere results in the formation of carbon monoxide and formic acid, a component of acid rain.

2.4 Methanol oxidation catalyst

A transition to methanol as a fuel for marine engines requires a new methanol oxidation catalyst (MOC). The MOC is placed between the engine and SCR, replacing the DOC used for diesel engines. The purpose of the MOC is, similar to a DOC, to convert harmful emissions into harmless products. Using methanol as a fuel, these emissions include CO, unburned methanol, formaldehyde, and other HCs. Due to difficulties with the operation of methanol fueled vehicles, the development of these, and thus the development of MOCs, has slowed down, and studies regarding methanol as a fuel alone and MOCs are limited [2]. There are mostly studies regarding diesel/methanol dual-fuels (DFs), which will be further analyzed.

2.4.1 Dual-fuel engines

One study by Yao *et al.* investigated how a diesel/methanol DF engine affected the exhaust emissions, compared to a diesel engine, both with and without an oxidation catalyst (OC) [2]. When using the DF engine without an OC, the smoke reduction is 50% compared to the diesel engine, while this increases to 80% with the addition of an OC. This could be due to methanol flame being smokeless and its rapid burning speed. Yao *et al.* also found that the NO_x emissions decreased using the DF engine. However, when adding the OC, there was a slight increase in NO_x emissions, indicating that unburned HCs and CO might cause the formation of NO_x.

2.4.1.1 CO and HC emissions

While the CO and HC emissions are higher when using the DF engine, the OC effectively reduces the levels for both compounds, below the levels of the diesel engine [2]. The level of emissions also depends on the fuel loading – a higher loading gives an increase in emission levels. CO emission formation is a result of improper mixing and incomplete combustion, and they are primarily controlled by the air/fuel equivalence ratio. In the DF engine, there is a lower gas temperature than in the diesel engine and thus a lower flame temperature, resulting in the formation of a thickened quench layer. The quench layer is a region near the combustion chamber walls where the temperature is lower, causing the combustion process to slow down. Additionally, the increased ignition delay in the DF engine causes an increase in CO emissions, since a portion of the fuel undergoes combustion during the expansion stroke, i.e., when the piston is moving down and delivering power. This decreases the gas temperature, and hence decreases the CO oxidation reaction rate, leading to incomplete combustion and consequently higher CO emissions. HC emissions are mainly caused by incomplete combustion, due to the lower gas temperature making it difficult to completely burn [16].

2.4.1.2 NO_x emissions

As previously mentioned, 90% of the NO_x emissions from a diesel engine is composed of NO. However, studies have found that in diesel/methanol compound combustion, the emissions of NO_2 can be significantly increased compared to when using only diesel [17]. A study by Lu *et al.* showed that a higher methanol concentration resulted in an increased NO_2/NO_x ratio [17]. This increase is due to the increased HO_2 free radicals produced by methanol during the combustion, which can then react with NO to produce NO_2, as shown in Reaction 2.16.

$$NO + HO_2 \longrightarrow NO_2 + OH \tag{2.16}$$

This phenomenon is significant for the following SCR, since large NO_2/NO ratios may result in uncertainty in the NO_x emission measurements in the SCR, with the most common measurement being developed for low NO_2/NO_x ratios [18]. However, in many cases the NO_2/NO_x ratio can be reduced using an OC, since NO_2 has strong oxidizing properties and may be used to oxidize other species [8, 18]. The ratio of NO_2/NO_x is also important for the NO_x reduction efficiency, where a 1:2 ratio of

NO_2/NO_x is optimal [19].

A common reaction of NO_x in the OC is the oxidation of NO to NO_2, as seen in Reactions 2.9-2.12. This reaction is kinetically limited at low temperatures while above 300°C, the reaction is limited by the thermodynamic equilibrium, where the maximum conversion is reached [8, 20]. In one study by Despres *et al.*, it was found that between 150°C and 300°C, the NO conversion to NO_2 increases with increasing concentrations of O_2 on a Pt/Al_2O_3 catalyst [20]. However, oxygen concentrations above 10% does not have a significant impact since the conversion remains almost constant [8, 20]. Another factor influencing the conversion is the concentration of the NO feed; a higher concentration gives a lower conversion of NO to NO_2 [20]. The conversion can also be decreased by the presence of H_2O, due to the competitive adsorption on the catalyst [8]. Additionally, NO_2 can react with nitrogen atoms to form N_2, according to Reaction 2.17 [21].

$$NO_2 + N \longrightarrow N_2 + O_2 \tag{2.17}$$

In a study by Salman *et al.*, it was found that the rate-determining step of NO oxidation is unlikely involving O_2 [8]. This is due to the higher activation energy barrier of the dissociative adsorption of O_2 compared to the adsorption of NO, which has no activation barrier. Instead, the rate-determining step is the desorption of NO_2, which could cause inhibition of the oxidation of NO to NO_2. On a Pt/Al_2O_3 catalyst, the NO_2 may even cause the formation of a platinum oxide (PtO) layer around the Pt core, which causes deactivation of the catalyst [20]. The NO_2 may also dissociate to NO and O_2 at temperatures above 200°C, at which the compound becomes unstable.

2.4.1.3 Methanol and formaldehyde emissions

The use of methanol as a fuel will also cause unburned methanol and formaldehyde emissions. The complete oxidation of methanol is as follows:

$$2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O \tag{2.18}$$

This reaction is highly exothermic with $\Delta H_{r(573K)}$= -1347 kJ/mol, giving an adiabatic temperature rise of approximately ΔT_{ad}= 46°C in the catalyst. The temperature rise is not an issue for the catalyst efficiency per se, but the SCR may struggle to efficiently operate at elevated temperatures [14].

One study by Chen *et al.* investigated the emissions characteristics of a diesel/methanol DF engine with a DOC [22]. As the ratio of methanol fuel increases, the unburned methanol emissions also increase. This is due to the the larger methanol heat absorption effect as the amount of methanol increases, resulting in the cylinder temperature to drop sharply. This decreases the flame propagation rate, resulting in some of the methanol discharging upon incomplete combustion or no combustion at all. Although the unburned methanol emissions are high, the DOC effectively treats this, with at least a 90% reduction. This reduction of emissions is not only a caused by the oxidation of methanol, it is also a result of the precious metals in

the DOC causing dehydrogenation of methanol, which results in the formation of formaldehyde, as well as methyl formate and CO:

$$CH_3OH \longrightarrow HCHO + H_2 \tag{2.19}$$

$$2\,CH_3OH \longrightarrow HCOOCH_3 + 2\,H_2 \tag{2.20}$$

$$CH_3OH \longrightarrow CO + 2\,H_2 \tag{2.21}$$

As the methanol ratio increases, the formaldehyde emissions also increase [22]. Formaldehyde emission formation is mainly caused by two factors: the interruption of methanol oxidation reaction within the combustion chamber due to low wall temperatures, and the oxidation of unburned methanol in the exhaust gas due to extended residence times and elevated oxygen levels. However, the addition of a DOC significantly decreases the formaldehyde emissions, mainly due to formaldehyde reacting with oxygen within the DOC:

$$HCHO + \frac{1}{2}\,O_2 \longrightarrow HCOOH \tag{2.22}$$

$$HCHO + O_2 \longrightarrow CO_2 + H_2O \tag{2.23}$$

Oxidation of unburned methanol, which increases the formaldehyde emissions, is simultaneously occuring in the DOC at lower exhaust gas temperatures [22]. If the formaldehyde production rate is greater than the consumption rate, this would lead to increased formaldehyde emissions. Hence the DOC could both promote or eliminate the formaldehyde formation, depending on the exhaust gas temperature.

2.4.2 Structure

The structure of a MOC has many similarities to that of a DOC, both featuring a substrate coated with a washcoat containing a support material and precious metals. Materials often used as supports for MOCs are insulating oxides, including SiO_2, Al_2O_3 and silica-alumina, but also zeolites and the graphite-like hexagonal boron nitride (hBN), while common precious metals used include Pt, Pd, and Rh [23], [24]. The selection of support material and precious metals significantly impacts the conversion efficiency of the catalyst, driving the necessity for the development of new oxidation catalyst specified for methanol fuels.

2.4.2.1 Support

In a study by Jeffrey *et al.*, the performance of a Pt/hBN catalyst was compared with that of a Pt/γ-Al_2O_3 catalyst [23]. The results show that the Pt/hBN catalyst achieves a 50% methanol conversion at room temperature, while 75°C is required for a 95% conversion. In contrast, the Pt/γ-Al_2O_3 catalyst requires significantly higher temperatures for similar levels of conversion: 110°C for 50% conversion and

approximately 170°C for 95% conversion. The high oxidation activity of the hBN-supported Pt-catalyst is a result of the weak bond between Pt and O on the hBN surface, resulting in high oxidation reactivity [23].

2.4.2.2 Precious metals — effect on exhaust emissions

The choice of metal and the gas composition present during catalysis are important factors determining the performance of a catalyst. In a study by Fujita *et al.*, the catalytic oxidation of unburned methanol in the presence of engine exhaust components from a methanol fueled engine was investigated [24]. The study focused on the effect of NO on the methanol oxidation using five different active metals: Pt, Pd, Rh, Ir and Cu.

The results show that the oxidation reaction temperature, the specific temperature at which an oxidation reaction occurs or is initiated, increases with increasing NO concentration for all catalysts tested, while the methanol oxidation reaction activity decreases [24]. How much the activity decreases depends on the type of catalyst, Pt being the least affected, followed by Pd, Rd, Ir, and Cu, being the most affected. Additionally, the formaldehyde formation significantly increases with increasing NO concentration for all of the tested catalyst. However, for the Pd-catalyst, the formation of formaldehyde is suppressed more than with the other catalysts, making it a good option for future methanol engine catalysts.

The effect of other methanol engine exhaust gases, including CO, H_2O, and HC, was also investigated for the Pt-catalyst [24]. The results reveal that the methanol oxidation temperature increases with increasing CO concentration, similar to NO. However, the temperature rise at equal concentrations of NO and CO is smaller for CO, indicating a lower effect on the oxidation of methanol. The effect of H_2O and HCs was very small, and differences in reaction temperature were hard to identify. The effects of CO, H_2O and propane on the formation of formaldehyde was also examined for the Pt-catalyst, showing significantly smaller impact than NO.

The amount of metal loading could also be an important factor for the conversion efficiency of unburned methanol and other engine emissions [24]. This was also investigated by Fujita *et al.* by testing three different loadings of Pt. For all loadings tested, the oxidation temperature increases while the catalytic activity decreases with increasing concentration of NO in the inlet gas mixture. Although there are differences in the reaction temperatures for the different amounts of loadings, these are small, indicating that the activity of a catalyst is not primarily determined by the amount of loading, but to a higher degree by the amount of NO present. The catalyst loading also has an impact on the formaldehyde formation; lower catalyst loading results in a higher formaldehyde formation, especially in the presence of NO.

3. Methods

3.1 Preparation of catalysts

3.1.1 Catalyst synthesis

In the synthesis of the catalysts, the wet incipient impregnation method was employed for the loading of Pt on the Al_2O_3 support. Before initiating the impregnation process, the Al_2O_3 was pretreated at 550°C, with a heating rate of 10°C/min, for 2 h in air.

For the 0.5 wt% loading, 0.17 g (≈100 µL) of $Pt(NO_3)_4$ precursor solution (15 wt% Pt) was poured into a glass vial. Ultrapure water was subsequently added to the vial to obtain a total volume of 2.75 mL, equal to the total pore volume of 5 g of the Al_2O_3 support. The pore volume was previously measured and determined by Ho *et al* [25]. The solution was sonicated for 2-3 min to ensure homogeneity of the solution. Following this, 5 g of the Al_2O_3 support was impregnated dropwise in a mortar. After each drop, the material was thoroughly mixed using a pestle. The impregnated material was dried at 80°C overnight, after which it was calcined at 550°C with a heating rate of 5°C/min for 2 h in air. The same process was repeated for 1.0 wt% and 1.5 wt% loadings respectively, as shown in Table 3.1.

Table 3.1: Pt-loading of the different catalysts in wt% and g/ft^3, and quantity of precursor solution used for each of the three catalysts in g and μL.

Pt loading [wt%]	Pt loading [g/ft^3]	Precursor sol. [g]	Precursor sol. [µL]
0.5	10	0.17	100
1	20	0.34	200
1.5	30	0.51	300

The Pt-loading of the three prepared catalyst samples was verified by ICP, and is shown in Appendix **??**.

3.1.2 Washcoating

2.1 cm (length) x 2.0 cm (diameter) (6.60 cm^3) honeycomb monoliths were used as substrates to coat the powdered material by using the dip-coating method. To prepare for the coating process, the bare monoliths were cut, after which they were calcined at 600°C for 2 h in air. Following this, a slurry was prepared by dissolving 95% catalyst powder and 5% P2 binder (boehmite) in a 1:1 solution of distilled H_2O and ethanol. The solution was stirred for 3-4 h, before coating the substrates. The monolith substrates were coated by dipping one end of the monoliths in the slurry, followed by drying the monoliths under a heating gun under constant movement, in

order to keep the liquid moving across all monolith pores and by this avoid clogging. This procedure was repeated until a total weight of 500 ± 10 mg coating was added to the monoliths. For each catalyst Pt loading, two slurries were prepared and two monoliths were coated, resulting in a total of 6 coated monoliths. After the washcoating, the monoliths were calcined at 550°C at a ramping rate of 5°C/min for 2 h in air.

3.1.3 Synthetic exhaust bench testing

3.1.3.1 Autotuning and calibration

Prior to the gas testing, autotuning and calibration were performed. Autotuning was used to fine-tune the heating of the reactor, while gas calibration was conducted to determine the FTIR-factor necessary for accurately measuring gas concentrations during the activity testing. The gas calibration was conducted in three separate sessions: calibration of H_2O, NO and NO_2, calibration of methanol, and calibration of CO and CO_2.

3.1.3.2 Degreening, pretreatment, and cycle testing

Degreening and pretreatment were performed before the activity testing for each of the catalysts. The pretreatment stabilizes the catalyst and prevents changes during the experiment, while the degreening removes water and organic substances from the catalyst. Additionally, three test cycles (T1, T2, and T3) were performed in order to determine the different temperatures for the activity testing. The test cycles were performed under a temperature range of 100°C to 500°C, with a temperature increase of 5°C/min. The gas composition and temperatures during the degreening, pretreatment, and test cycles are described in Table 3.2.

Table 3.2: Composition of gases, residence time, and temperatures used in the degreening, pretreatment, and cycle tests.

Test	Temperature [°C]	Time [min]	NO [%]	H_2 [vol%]	MeOH [%]	O_2 [vol%]	H_2O [vol%]
Degreening	550	30		0.9			5
Degreening	700	120				10	5
Pretreatment	500	60	0.05			10	5
T1	100	60			0.1	10	5
	500	30			0.1	10	5
T2	100	60			0.1	10	5
	500	30			0.1	10	5
T3	100	60			0.1	10	5
	500	30			0.1	10	5

3.1.3.3 Activity testing

Based on the results obtained from the test cycles, the temperatures chosen for the activity testing were 120°C, 200°C, and 300°C.

Table 3.3: Composition of gases and residence time for the activity testing at 120°C.

Temperature [°C]	Time [min]	NO [%]	NO_2 [%]	MeOH [%]	O_2 [vol%]	H_2O [vol%]
500	60				10	5
120	30				10	5
120	120			0.1	10	5
120	120	0.05		0.1	10	5
120	120			0.1	10	5
120	120		0.05	0.1	10	5
120	120			0.1	10	5
120	120	0.025	0.025	0.1	10	5
120	120			0.1	10	5

To examine the impact of each temperature on methanol conversion, three separate test runs were conducted for each of the three catalysts, according to the test plan for 120°C in Table 3.3. During each test, NO, NO_2, and a 1:1 mixture of NO and NO_2 were introduced into the feed to investigate their influence on methanol conversion, as well as on the formation of formaldehyde and CO_2. The space velocity used for the three tests was 25 000 h^{-1}. The test plan for 200°C and 300°C in Appendix C.1 and C.2 are similar to the 120°C test plan, with the only difference being the temperature.

4. Results and Discussion

4.0.1 Cycle testing

During the test cycles, the reactor temperature (T_r) and catalyst temperature ($_c$) were measured, and a comparison is shown in Figure 4.1. For the 0.5 and 1.0 wt% catalysts, the catalyst temperature is approximately 517°C and 519°C, respectively, indicating a temperature increase caused by the methanol oxidation being an exothermic reaction, of which the adiabatic temperature for complete methanol oxidation was calculated to 46°C. The temperature profile of the 1.5 wt% loading is different from the 1.0 and 0.5 wt%, as it shows a decreased catalyst temperature in comparison to the reactor temperature, however, the reason for this is unclear.

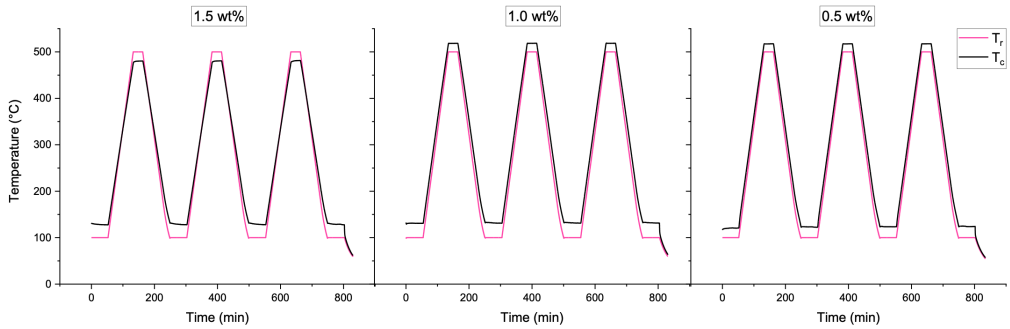

Figure 4.1: Reaction and catalyst temperature for 1.5, 1.0, and 0.5 wt% Pt-loading.

The result from the measurements of the CO_2, methanol and formaldehyde concentrations, together with reactor temperature, is shown in Figure 4.2. For 1.5 and 1.0 wt% loading, a full conversion of methanol and no formation of formaldehyde is seen, resulting in a constant concentration of CO_2 throughout the experiment. In contrast, the result of the 0.5 wt% loading shows small deviations in the methanol oxidation, as it reveals that methanol is not completely oxidized at the point where the temperature reaches 100°C, which is also indicated by the decrease in CO_2 concentration. At this temperature, a formation of formaldehyde is also observed. The result indicates that the formation of formaldehyde is temperature-dependent, where 100°C is a distinct breaking point.

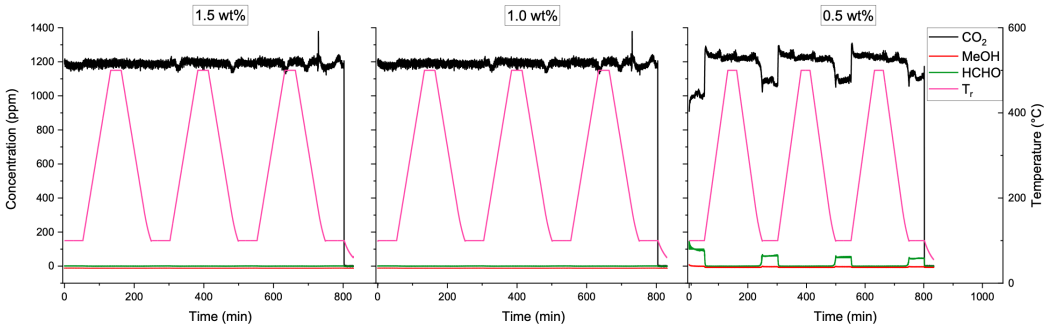

Figure 4.2: Reaction temperature and concentration of CO_2, MeOH, and HCHO for 1.5, 1.0, and 0.5 wt% Pt-loading.

4.0.2 Activity testing

During the activity testing, the methanol concentration at higher temperatures is zero or close to zero, which can be observed in Figure 4.3. The breaking point for the full conversion of methanol is approximately 200°C, where the methanol concentrations increase when NO_x is included in the feed. However, at 120°C, the methanol concentration is significantly higher than at 200°C and 300°C. This could be due to the NO being more readily adsorbed on the catalyst surface at 120°C, leaving a limited space for the O_2 to adsorb on the surface, consequently preventing methanol oxidation. At 200°C and 300°C, O_2 is more readily adsorbed on the catalyst surface, giving a higher conversion of methanol. Other possible reasons for the low methanol conversion could be the water adsorbing on the catalyst surface and blocking the active sites, as well as the O_2 being used in the NO and formaldehyde oxidation.

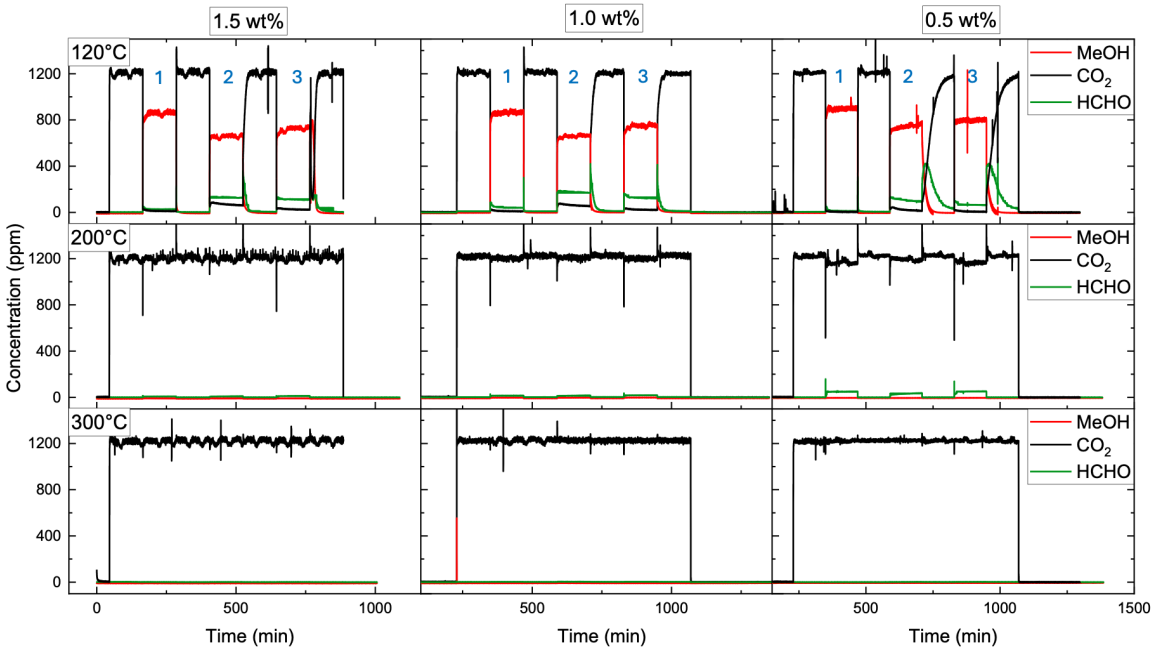

Figure 4.3: Concentration of MeOH, CO_2, and HCHO for 1.5, 1.0, and 0.5 wt% Pt-loading at 120°C, 200°C, and 300°C. The feed is composed of 1000 ppm methanol, 5% H_2O, and 10% O_2. In period 1, 2, and 3, an additional feed of 500 ppm NO, 500 ppm NO_2, and a mixture of 250 ppm NO and 250 ppm NO_2, respectively, is added.

The result also shows that at 120°C, below the limit for full conversion of methanol, the degree of conversion is highly dependent on the presence of NO_x, specifically NO_2. For 120°C, seen in Figure 4.4, a higher methanol conversion is observed when NO_2 is added to the system. This could be explained by NO_2 being a strong oxidizing agent, hence contributing to the oxidation of methanol. The loading also affects the conversion of methanol, where an increasing loading gives a higher conversion due to more active sites being available. This is seen in Figure 4.3, where the concentration of methanol is lower for 1.0 and 1.5 wt% at 120°C, than it is for 0.5 wt%.

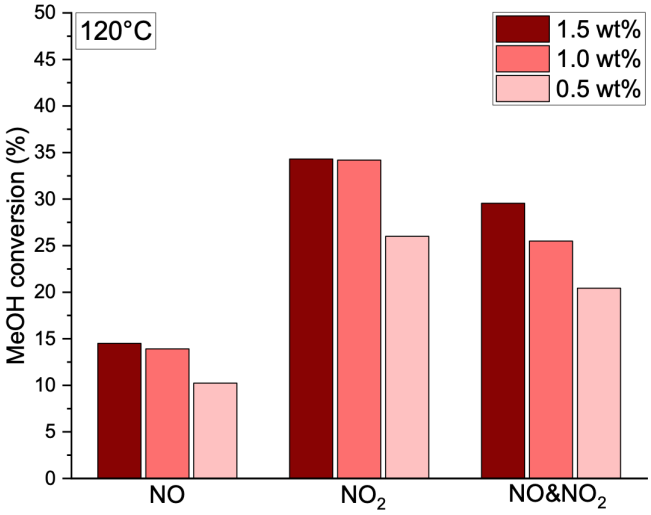

Figure 4.4: Conversion of methanol for 0.5, 1.0, and 1.5 wt% Pt-loading for the different NO_x feeds at 120°C. In periods marked NO, NO_2, and NO&NO_2, an additional feed of 500 ppm NO, 500 ppm NO_2, and a mixture of 250 ppm NO and 250 ppm NO_2, respectively, is added to the standard feed.

In alignment with the cycle testing, the result from the activity testing shows that the formation of formaldehyde is temperature-dependent. In Figure 4.3, at 300°C, the concentration of formaldehyde is zero, while at 200°C small amounts of formaldehyde is formed. At 120°C, where the methanol conversion is low, a significantly higher amount of formaldehyde is visible for all three loadings. In addition, the result also shows that the formation of formaldehyde is dependent on the presence of NO_x. A higher formaldehyde formation is seen in period 2 and 3, where NO_2 is included in the feed, indicating that NO_2 increases the formation of formaldehyde. In period 1, no or little formation of formaldehyde is observed, which could be caused by the NO oxidation to NO_2, which is limited for period 1.

Comparing the formaldehyde formation for the different loadings of Pt, some minor differences are observed. At 200°C, a slightly higher formation of formaldehyde can be seen for the 0.5 wt% loading. This could be caused by the lower loading offering fewer active sites for the direct methanol oxidation, resulting in breakdown of methanol to formaldehyde. Another possible explanation is that with fewer active sites, the oxidation of formaldehyde is hindered, giving higher concentrations of formaldehyde left in the system. However, at 120°C, the 0.5 wt% loading has a lower formation of formaldehyde than 1.0 and 1.5 wt%, which could be caused by the lower methanol conversion.

Upon closer analysis of 120°C in Figure 4.3, a formaldehyde peak and a slower increase of CO_2 can be observed for 0.5 wt% compared to the other two loadings, which is apparent Figure 4.5. This is most likely due to NO_2 causing PtO formation, which in turn deactivates the catalyst. Without the NO_x feed, the catalyst is approaching recovery, however, even after 2 h, full recovery cannot be reached. The same phenomenon can be observed for 1.0 and 1.5 wt% at 120°C, although

the peaks are not as pronounced as in 0.5 wt% and the recovery is relatively rapid. This is due to the 0.5 wt% loading having fewer active sites than 1.0 and 1.5 wt% loadings, which will be blocked by the PtO formation.

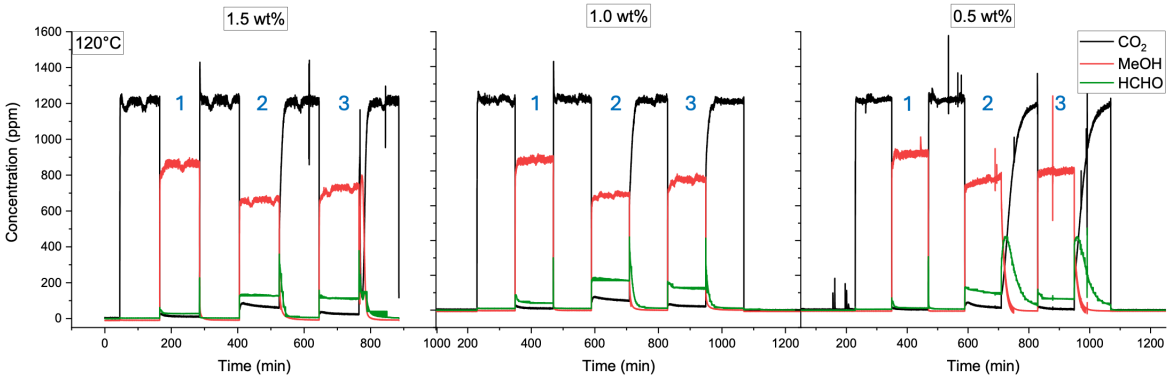

Figure 4.5: Concentration of MeOH, CO_2, and HCHO for 1.5, 1.0, and 0.5 wt% Pt-loading for 120°C. The feed is composed of 1000 ppm methanol, 5% H_2O, and 10% O_2. In period 1, 2, and 3, an additional feed of 500 ppm NO, 500 ppm NO_2, and a mixture of 250 ppm NO and 250 ppm NO_2, respectively, is added.

It can also be observed in Figure 4.5 that when the methanol conversion is low, the CO_2 concentration is also low, leading to a carbon imbalance between the gas inlet and outlet. This could either indicate that non-detectable carbon-containing intermediates have been formed, or it could be caused by measurement errors of the FTIR. Given that the FTIR is not calibrated for formaldehyde, the measurements could result in lower values than the actual outlet concentrations.

The concentration of NO and NO_2 throughout the activity testing was measured and is presented in Figure 4.6. The result reveals that at the higher temperatures, more NO is oxidized to NO_2. The NO_2 concentration is also higher with increasing loading. At 120°C however, this does not seem to be the case. In the first period, NO is not oxidized to NO_2 at all, for any of the loadings. In the second and third period, the NO_2 is increasing with decreasing loading. This phenomenon is due to a transient period, which is caused by the NO_2. As previously mentioned, NO_2 causes the formation of PtO, which can result in this slow transient. However, the transient can also be due to the NO_2 reacting with accumulated intermediates on the catalyst surface. While the concentrations of NO and NO_2 for 1.5 and 1.0 wt% are similar, the 0.5 wt% loading shows a deviating behavior. This is due to the 0.5 wt% having fewer active sites, meaning that the formation of PtO will have a more significant impact on the activity of the catalyst. This limits the oxidation of methanol by NO_2, hence resulting in higher concentrations of NO_2 for the 0.5 wt% loading.

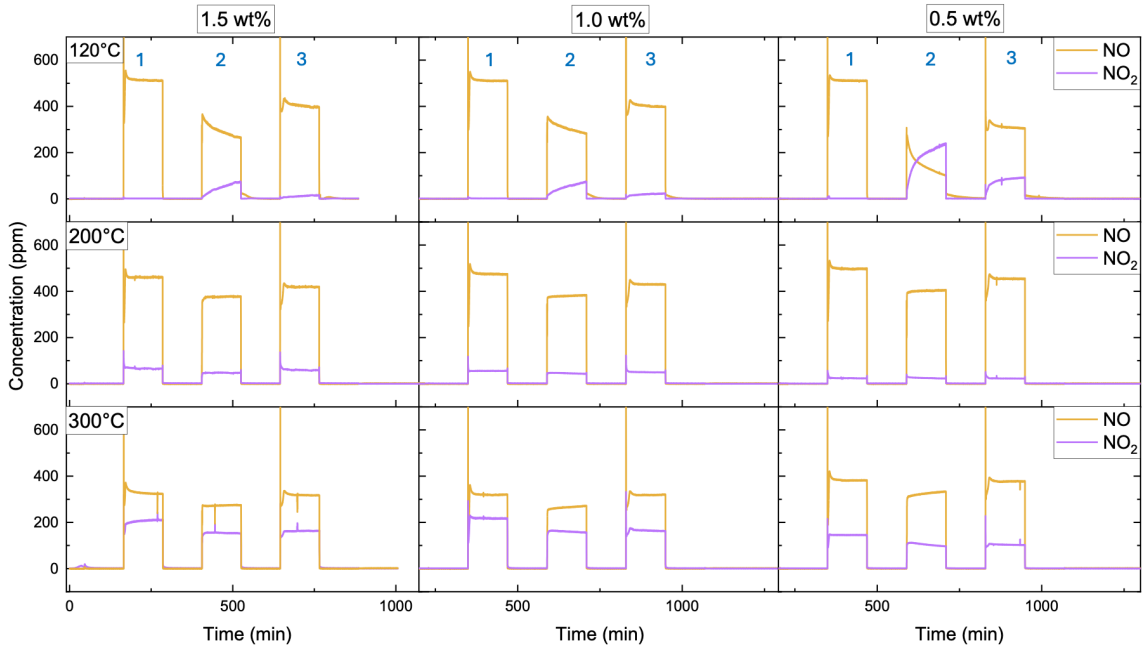

Figure 4.6: Concentration of NO and NO_2 for 1.5, 1.0, and 0.5 wt% Pt-loading. The feed is composed of 1000 ppm methanol, 5% H_2O, and 10% O_2. In period 1, 2, and 3, an additional feed of 500 ppm NO, 500 ppm NO_2, and a mixture of 250 ppm NO and 250 ppm NO_2, respectively, is added.

When NO_2 is introduced to the feed, it can clearly be seen in Appendix D.1 that some N-species, other than NO, has formed since the total 500 ppm of NO and NO_2 is not reached. It can also be observed that a lower reaction temperature, a lower loading, and a higher NO_2 feed is increasing the formation of unknown N-species. One N-species that was measured during the experiments was N_2O, however, the concentration of this compound remained at a constant zero, and was thus not produced. The unknown N-species could instead be N_2, which can be formed by the reaction of NO_2 and N according to Reaction 2.17.

Comparing the NO_x results in Figure 4.6 with the theoretical equilibrium, some notable differences emerge. According to equilibrium of the NO to NO_2 reaction in Appendix E.1, at 120°C and 200°C, there should be 100% conversion to NO_2, while 80% NO_2 is present at 300°C. However, the results in Figure 4.6 do not correspond to the equilibrium. At higher temperatures and higher loadings, more NO is oxidized to NO_2, whereas the opposite trend is observed in Appendix E.1.

The temperature and loading effect on NO_x is further examined in Figure 4.7, which presents the ratio of NO_2/NO_x for the different loadings at 120°C, 200°C, and 300°C. Generally, it can be observed that the NO_2/NO_x ratio is lower than the optimal NO_2/NO_x ratio of 0.5 for the SCR, which decreases the SCR efficiency. For the 1.0 and 1.5 wt% loading at 300°C, the NO_2/NO_x ratio is closest to 0.5, however, this ratio could potentially further increase and thus decrease the SCR efficiency at higher temperatures and loadings. While this increase can be observed for the 0.5 wt% loading at 120°C where the ratio is approximately 0.6, this increase is caused

by the slow transient previously discussed. Additionally, regardless of the NO_x inlet, the NO_2/NO_x ratio is approximately the same for each loading respectively. This is however only true when the temperature is 200°C and 300°C, having full conversion of methanol.

Comparing the results in Figure 4.7 with the equilibrium NO_2/NO_x ratio at 120°C, 200°C, and 300°C in Appendix E.2, the ratio of NO_2/NO_x at 300°C should be 0.87, while the actual ratio is between approximately 0.2 and 0.4, depending on loading. When comparing the actual and equilibrium ratios at 200°C and 120°C, even larger differences are observed, where the NO_2/NO_x ratio is minimal for 120°C with only NO feed, when it should be 1.0 according to equilibrium.

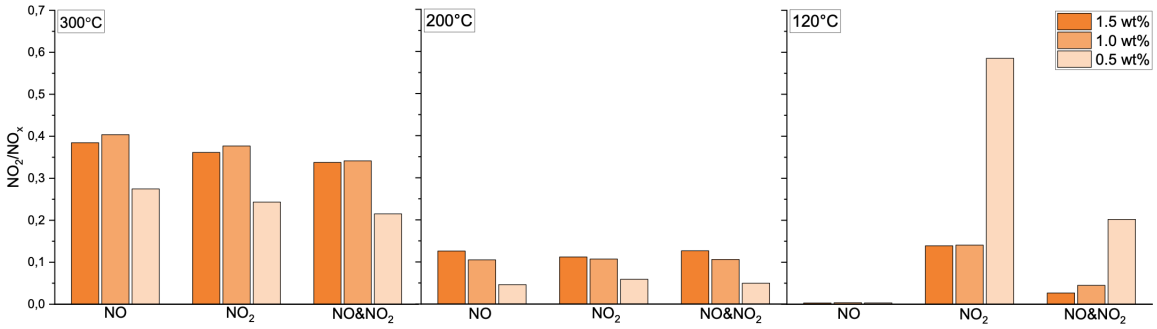

Figure 4.7: NO_2/NO_x for 1.5, 1.0, and 0.5 wt% Pt-loading at 300°C, 200°C, and 120°C for the different NO_x feeds.The feed is composed of 1000 ppm methanol, 5% H_2O, and 10% O_2. In periods marked NO, NO_2, and NO&NO_2, an additional feed of 500 ppm NO, 500 ppm NO_2 and a mixture of 250 ppm NO and 250 ppm NO_2, respectively, is added.

The reason for the differences is the reaction kinetics limiting the reaction rates; at high temperatures and high catalyst loadings, higher reaction rates are favored. This can be observed for 1.0 and 1.5 wt% loading at 300°C in Figure 4.7, where the reaction is the closest to equilibrium. At 120°C and 200°C, the reaction rates are slow, causing large deviations from equilibrium. Moreover, there are differences in the reaction conditions of the equilibrium and the results in Figure 4.6 and 4.7. In the equilibrium, 10% O_2 is present while in the bench test, additional 5% H_2O and 1000 ppm methanol are also present. Since NO_2 is a strong oxidizing agent, stronger than O_2, NO_2 will be consumed in the methanol oxidation, as previously discussed for Figure 4.3. This could explain why equilibrium is not reached even at 300°C.

5. Future Work

For a future implementation of methanol as a fuel for marine engines, further studies need to be performed on the catalyst performance under different conditions. The findings of this study have given rise to several suggestions of what could be further investigated, which are presented below.

- To optimize the catalysts used for future methanol engines, the choice of precious metals needs to be further investigated. A suggestion for future studies is to test Pd, as well as a combination of Pd and Pt. This is based on the study by Fujita *et al.*, finding that Pd is the precious metal, out of five tested, that is the least affected by activity degradation in the presence of NO, as well as the catalyst that to the highest degree suppressed the formation of formaldehyde.
- Another important factor to consider in future studies is the NO/NO_2 ratio of the inlet feed. As the result have shown that NO_x, particularly NO_2, highly affects the conversion of methanol as well as the formation of formaldehyde, further studies would need to be performed to find the optimal gas composition that could help increase the conversion of methanol, while minimizing the formaldehyde formation.
- To investigate what reactions are occurring, the gases used in this experiments could be individually run. Particularly, it would be interesting to conduct a test with methanol in absence of oxygen, to conclude the extent of formaldehyde formation resulting from methanol degradation at the different loadings and temperatures. This would give further insights on what factors affect the formation of formaldehyde, and how this formation can be minimized.
- The gases tested in this experiment could also be run over a bare monolith, to investigate what gas phase reactions are occurring in addition to the catalyzed reactions. This could give a better understanding of intermediate formation and degradation of methanol.
- By testing more temperatures between 120°C and 300°C, critical temperatures for formaldehyde formation and methanol conversion can be obtained.
- The space velocity used in the experiments was relatively low, compared to the space velocity generally used in maritime transportation. Hence higher space velocites can be tested in order to see the effect on the oxidation of methanol as well as the formation of formaldehyde.
- A longer running time can be kept, both when NO_x is included and excluded in the feed, to observe the effect on the activity of the different Pt-loadings.
- Different H_2O concentrations can be tested to investigate the effect of water on catalyst deactivation, and hence the conversion of methanol.

6. Conclusion

Through syngas bench testing of three catalysts with varying loadings of Pt on Al_2O_3 support (0.5 wt%, 1.0 wt%, and 1.5%), along with investigating the impact of NO and NO_2 on methanol oxidation and formaldehyde formation, several key findings have been revealed.

Temperature dependency was evident, with complete methanol oxidation to CO_2 starting at 100°C without NO_x and around 200°C with NO_x. Lower temperatures and lower catalyst loadings resulted in decreased methanol conversion, highlighting the importance of optimal operating conditions for efficient oxidation. Additionally, methanol conversion decreased with the presence of NO_x, with the lowest conversion observed when only NO was fed. The presence of NO_2 increased methanol conversion compared to NO due to its strong oxidizing properties, further highlighting the complex interplay between NO_x and methanol oxidation. Furthermore, the presence of NO_2 also increased formaldehyde formation and caused catalyst deactivation at low temperature, indicating its significant role in the oxidation process. The catalyst loading however, showed a minor impact on the formation of formaldehyde. Another notable finding was that the NO_2/NO_x ratio may be a concern for the SCR, especially if it further increases at higher temperatures. Also, regardless of the NO_x inlet, NO_2/NO_x ratio is approximately the same for the different Pt-loadings respectively. Generally, the 1.5 and 1.0 wt% loadings showed similar behavior, while the 0.5 wt% loading exhibited significant deviations, with a higher degree of deactivation at low temperature. According to this study, the 1.0 wt% Pt-loading catalyst is hence the most interesting catalyst. Having almost the same performance as the 1.5 wt%, while still needing less Pt, this would be more economically favorable. Additionally, the 1.0 wt% had significantly better performance than the 0.5 wt%, which was more readily deactivated as lower temperatures.

These findings provide valuable insights into the performance of MOC coatings and contribute to the ongoing efforts in developing cleaner and more efficient marine methanol engines. Further research in this area could focus on optimizing catalyst formulations and operating conditions to reduce emissions from marine engines.

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A. Appendix 1

In this section the calculations for the adiabatic temperature rise (ΔT_{ad}), caused by the oxidation of 1000 ppm methanol (Reaction A.1), are shown.

$$2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O \tag{A.1}$$

The equation for ΔT_{ad} is as follows:

$$\Delta T_{ad} = X_A \cdot F_{A0} \cdot \Delta H_r \,/\, (F_tot \cdot C_p) \tag{A.2}$$

Where X_A is the fractional methanol conversion, F_{A0} is the feed molar flow rate of methanol, F_{tot} is the total molar flow rate of stream flowing through the reactor, ΔH_r is the enthalpy change at 300°C, and C_p is the average molar heat capacity of stream flowing through the reactor. Since ΔH_r varies with temperature, ΔH_r at 300°C must be calculated according to Section A.1.

The volumetric flow rate is 2750 mL/min, from which F_{tot} is calculated to 0.1143 mol/min. Having 1000 ppm methanol, F_{A0} is then $0.001F_{tot}$. Assuming that all the methanol is fully converted and that C_p is 29 J/molK, ΔT_{ad} is calculated to 46°C:

$$\Delta T_{ad} = 1 \cdot 0.001 \cdot 0.1143 \cdot -1347.27 \cdot 10^3 \,/\, (0.1143 \cdot 29) = -46.46\,^{\circ}C \tag{A.3}$$

A.1 Calculation of $\Delta H_{r(573K)}$

Table A.1 shows the regression coefficients A, B, C, D, and E for the different gases, obtained from Chemical Properties Handbook, 1st Edition by Carl L. Yaws (ISBN: 9780070734012). C_p for each of the compounds can also be seen in Table A.1 and is calculated according to Equation A.4.

$$C_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4 \tag{A.4}$$

$C_{p(tot)}$ is then calculated to 16.57 J/molK:

$$C_{p(tot)} = (2\,C_{p(CO)} + 4\,C_{p(H2O)}) - (2\,C_{p(MeOH)} + 3\,C_{p(O2)}) \tag{A.5}$$

Table A.1: The regression coefficients and the calculated C_p for the different gases at 300°C.

	A	B	C	D	E	$C_{p(573K)}$ [J/mol K]
MeOH	40.046	-3.8287E-02	2.4529E-04	-2.1679E-07	5.9909E-11	64.3163
O_2	29.526	-8.8999E-03	3.8083E-05	-3.2629E-08	8.8607E-12	31.7467
CO_2	27.437	4.2315E-02	-1.9555E-05	3.9968E-09	-2.9872E-13	45.9827
H_2O	33.933	-6.4186E-03	2.9906E-05	-1.7825E-08	3.6934E-12	37.1188

$\Delta H_{r(295K)}$ is -1351.88 kJ/mol from which $\Delta H_{r(573K)}$ is calculated to -1347.27 kJ/mol:

$$\Delta H_{r(573K)} = \Delta H_{r(295K)} + C_{p(tot)} \cdot \Delta T = -1351.88 + 16.57 \cdot (573\text{-}295) = -1347.27\,\text{kJ/mol} \tag{A.6}$$

B. Appendix 2

Table A.1 shows the expected Pt-loadings in wt% and mg/kg, as well as the actual Pt-loadings verified by ALS Scandinavia AB Luleå.

Table B.1: Expected catalyst loadings in wt% and mg/kg, and actual Pt-loadings in mg/kg.

Pt-loading [wt%]	Pt-loading [mg/kg]	Pt-loading [mg/kg]
0.5	5 000	5 010
1	10 000	10 100
1.5	15 000	14 600

C. Appendix 3

Table C.1 and C.2 show the composition of gases, temperatures and residence times used for the activity testing.

Table C.1: Composition of gases and residence time for the activity testing at 200°C.

Temperature [°C]	Time [min]	NO [%]	NO_2 [%]	MeOH [%]	O_2 [vol%]	H_2O [vol%]
500	60				10	5
200	30				10	5
200	120			0.1	10	5
200	120	0.05		0.1	10	5
200	120			0.1	10	5
200	120		0.05	0.1	10	5
200	120			0.1	10	5
200	120	0.025	0.025	0.1	10	5
200	120			0.1	10	5

Table C.2: Composition of gases and residence time for the activity testing at 300°C.

Temperature [°C]	Time [min]	NO [%]	NO_2 [%]	MeOH [%]	O_2 [vol%]	H_2O [vol%]
500	60				10	5
300	30				10	5
300	120			0.1	10	5
300	120	0.05		0.1	10	5
300	120			0.1	10	5
300	120		0.05	0.1	10	5
300	120			0.1	10	5
300	120	0.025	0.025	0.1	10	5
300	120			0.1	10	5

D. Appendix 4

Figure D.1 shows the theoretical nitrogen balance, based on the measured concentrations of NO and NO_2 out of the catalyst.

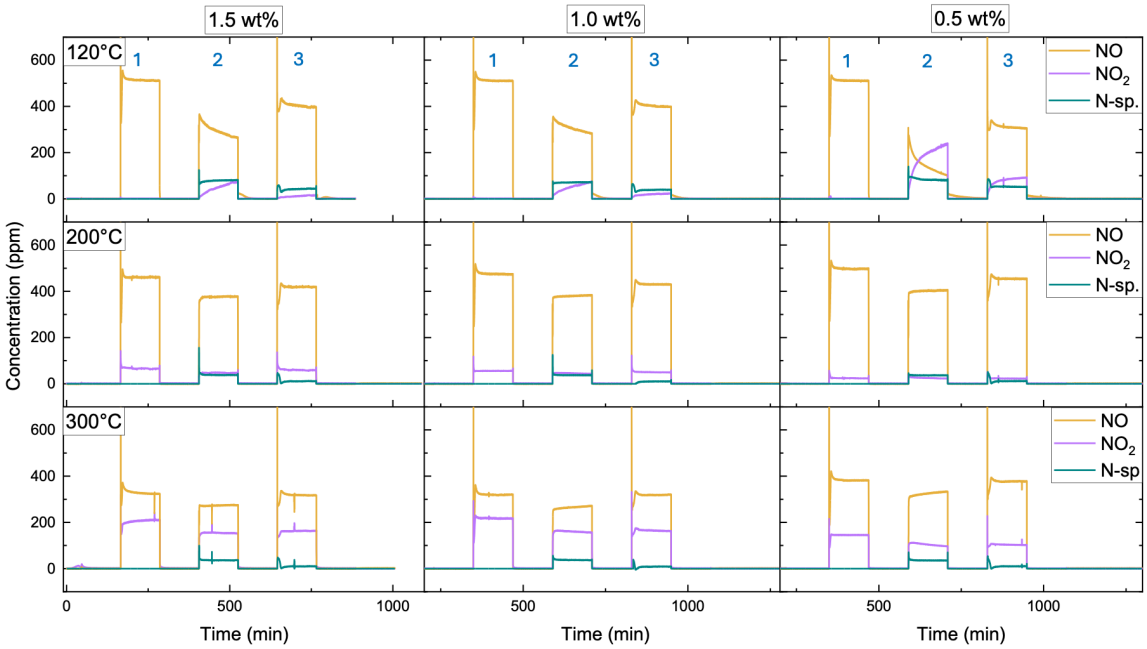

Figure D.1: Concentration of NO, NO_2, and N-species for 1.5, 1.0, and 0.5 wt% Pt-loading.

E. Appendix 5

Figure E.1 represents the theoretical equilibrium of Reaction E.1 at 500 ppm NO, while Figure E.2 shows the calculated mean NO_2/NO_x ratio at 120°C, 200°C and 300°C, based on the measured concentrations of NO_2 and total NO_x for the three different loadings at each temperature.

$$NO + \frac{1}{2} O_2 \longrightarrow NO_2 \tag{E.1}$$

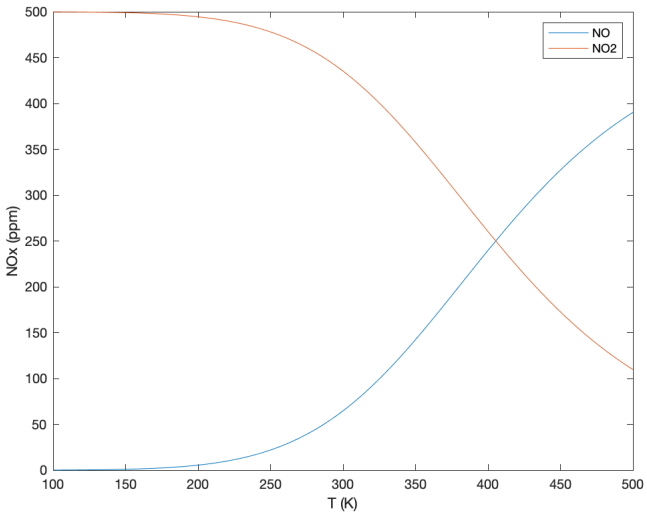

Figure E.1: Theoretical equilibrium for 500 ppm NOx.

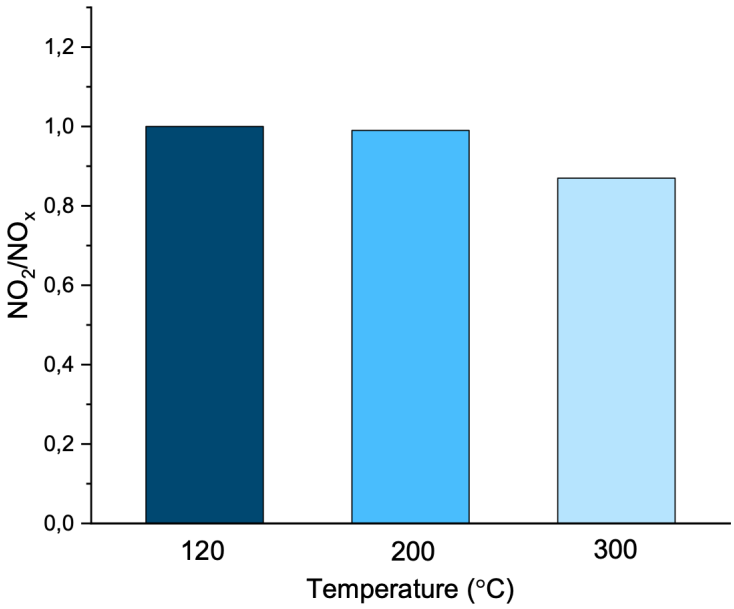

Figure E.2: Mean NO_2/NO_x ratio at 120°C, 200°C and 300°C.

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