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Hydrogenolysis of methyl formate over copper nano particles

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Abstract

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Abstract:

Hydrogenolysis of methyl formate has been proposed as a part of an alternative route for methanol production. Copper catalyst for the hydrogenation of ester to alcohol is a catalyst commonly used due to its high selectivity and conversion for alcohol. The focus in this work is to see the performance of nanoparticle copper catalyst, for hydrogenolysis of methyl formate at different temperature. Nano sized metal catalyst has been discovered to have improved efficiency, selectivity and stability. Two types of nanoparticle catalyst have been tested, Cu_2O and CuO, where CuO has a smaller crystallite and particle size than Cu_2O. The catalyst has been tested in a low-pressure gas phase reaction for hydrolysis of methyl formate to methanol at 170°C, 210° and 250°C. In the experimental work, the conversion showed to increase with higher temperature, and the highest conversion was found at 250°C. The catalyst with the smallest crystallite and particle size had the highest conversion of 76%, at 250°C. In the reaction at 250°C the formation of CO increase compared to the reaction at 170°C and 210°C. Because of the increased formation of CO, the selectivity to methanol was 78% at 250°C, while at 170°C and 210°C the selectivity to methanol was 90%.

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Nomenclature

Symbol	Definition
F	Flow
HSE	Health, safety and environment
K	Equilibrium constant
P	Absolute pressure
p_i	Partial pressure of a specie
p_i°	Vapor pressure of a specie
T	Temperature
TEM	Transmission electron microscopy
USN	University College of Southeast Norway
XRD	X-ray diffraction
Y	Mole%
y_i	Molar fraction of a specie

Preface

The University College of Southeast Norway (USN) assigned me this Mater Thesis, and provided me with a process rig and necessarily equipment for the experimental work. The experimental work has been carried out in the high performance liquid chromatography (HPLC) laboratory in the process hall at USN.

This study has it focus on copper nanoparticles catalysis performance at varied temperature, for gas- phase hydrolysis of methyl formate.

I would like to thank my supervisor Christian Ahoba-Sam for all his help and guidance through the challenge of the experimental part, providing me with the catalyst used for testing, and for valuable discussion on my result through the thesis. I would also like to thank my other supervisor Klaus-Joacim Jens for guidance and valuable discussion on my result through the thesis.

At last, I will thank my family for all there help and support during this period.

Porsgrunn, 09. Juni 2016

Hilde Hauge Amundsen

1 Introduction

Methanol is a potential fuel, energy storage and feedstock for synthetic hydrocarbon, and can replace or take over partly for fossil fuel in the future. The production of methanol are commonly from synthesis gas (syngas) consisting of carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2).[1] Industrial the production of methanol are usually from synthesis gas over Cu/Zn catalyst with pressure around 100 bar and temperature of 250°C, there is a lasting interest of finding a milder way for methanol production.[2] The synthesis of methanol was reported by Christiansen in 1919[3], the reaction has two step. In the first reaction (R1-1) methyl formate is formed, and in the second reaction (R1-2) methanol is formed.

$$CO + CH_3OH \leftrightarrow HCOOCH_3 \qquad\qquad \text{(R1-1)}$$

$$HCOOCH_3 + 2H_2 \leftrightarrow 2CH_3OH \qquad\qquad \text{(R1-2)}$$

Hydrogenolysis of methyl formate has been proposed as a part of an alternative route for methanol production[4] Copper catalyst for the hydrogenation of ester to alcohol is a catalyst commonly used due to its high selectivity and conversion for alcohol.[2] From an industrial and economical point of view, nano sized metal catalyst has been discovered to have improved efficiency, selectivity and stability.[5] Compared to larger particles catalyst, nanoparticles often have catalytic properties high above or sometimes new due to their nano size. The small particle size gives them higher surface to volume ratio and chemical potential.[6]

The focus in this work is on the second reaction, hydrolysis of methyl formate to methanol, reaction (R1-2). The hydrolysis is in a low-pressure gas-phase reaction over a copper catalyst. The purpose is to look at a new ways to form methanol more economical. Copper is a commonly used catalyst for hydrolyzing of ester due to its characteristic, but the effect of nanoparticle sized catalyst compared to larger is unknown. In the experimental part, two different types of copper nanoparticle catalyst with different pore size is used, catalyst Type (I) Cu_2O and Type (II) CuO. The catalyst has been tested at different temperature to see how temperature effect conversion, selectivity to methanol and deactivation of the catalyst.

2 Theory

This chapter includes reaction of methyl formate and the equilibrium constant for the hydrolysis. The surface, adsorption and deactivation of a catalyst is also in this part, as well as equipment used for analyzing the product stream.

2.1 Hydrogenolysis of methyl formate

In the reaction, hydrogenolysis of methyl formate, hydrogen break up the bond between carbon and oxygen, and form C-H and O-H bond. Reaction (R2-1) show the main hydrolysis of methyl formate to methanol reaction, this reaction is reversible.[7]

$$HCOOCH_3 + 2H_2 \leftrightarrow 2CH_3OH \tag{R1-2}$$

While the primary reaction of methyl formate converting to methanol, undesired side reaction might occur. The reaction mixture could have different components. This side reaction from methyl formate, lowers the selectivity to methanol. In reaction (R2-1) CO and methanol is formed, while CO_2 and methane is formed in reaction (R2-2). In reaction (R2-3) carbon and water are formed, and reaction (R2-4) form formaldehyde. These are possible side reaction methyl formate can undergo.[7]

$$HCOOCH_3 \rightarrow CO + CH_3OH \tag{R2-1}$$

$$HCOOCH_3 \rightarrow CO_2 + CH_4 \tag{R2-2}$$

$$HCOOCH_3 \rightarrow 2C + 2H_2O \tag{R2-3}$$

$$HCOOCH_3 \rightarrow 2CH_2O \tag{R2-4}$$

Reaction (R2-5) two mole of methyl formate forms CO_2, formaldehyde and dimethyl ether is formed.

$$2HCOOCH_3 \rightarrow CO_2 + CH_2O + CH_3OCH_3 \tag{R2-5}$$
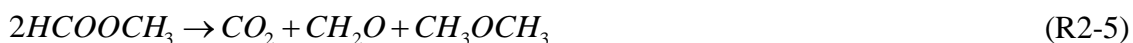
Reaction (R2-6) is another hydrolysis reaction of methyl formate that can take place. Formaldehyde from reaction (R2-6), can further react in reaction (R2-7), and form CO and H_2.[7]

$$HCOOCH_3 + H_2 \rightarrow CH_2O + CH_3OH \tag{R2-6}$$

$$CH_2O \rightarrow CO + H_2 \tag{R2-7}$$

2.2 Thermodynamics

When a reactant is converted to a product with a chemical reaction, the rate and the equilibrium conversion depends on pressure, temperature and the reactants composition. Often a catalyst suited for the reaction is needed to have a sensible reaction rate. Calculated equilibrium conversion is the highest possible conversion and do not depend on reaction rate or catalyst [8] Often the reaction rate increase with increased reaction temperature. A rule of thumb, is the reaction rate doubles for every 10°C increase in temperature.[9]

The equilibrium reaction of the hydrolysis of methyl formate is pressure and temperature dependent. This means that composition of the reaction mixture at equilibrium can be estimated from thermodynamics law. Hydrogenolysis of methyl formate to methanol is an exothermic reaction and release heat. [7] The equilibrium between methyl formate and methanol was investigated by Christiansen [10] in 1926, the equilibrium constant (K) expressed in equation (2-1) was found to be dependent on the temperature (T) in Kelvin.

$$\log K = -\frac{3016}{T} + 3{,}61 \qquad\qquad (2\text{-}1)$$

2.3 Catalyst

The definition of a catalyst is that a catalyst makes a reaction occur faster with less activation energy than an uncatalysed reaction, this without being consumed in the process. Catalyst is important for the industry and used in a wide range of processes.[11]

For heterogeneous catalyst, the reactants are often in gas form and the catalyst in solid. The surface of a catalyst is not uniform and metal crystal has an abrupt transition in step. The surface of catalyst Type (I) Cu_2O used in this work, obtained from C. Ahoba-Sam, is shown in Figure (2-1). Atoms in the uneven points at the surface are not completely coordinated, this gives them the possibility to interact with incoming molecules. It is often in this point the reaction happens. The surface of the heterogeneous catalyst is important, for the efficiency of a catalyst. It is not only the surface area but also the composition and the structure that is important for a catalyst. Activity, selectivity and stability for the catalyst depend on interaction on the surface.[12]
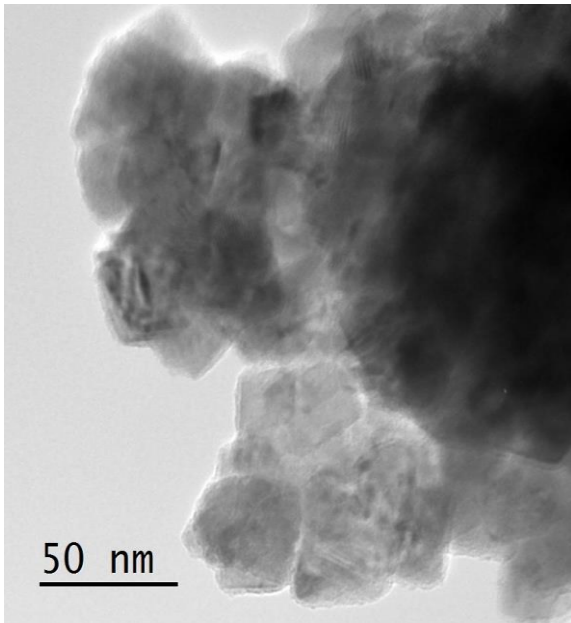
Figure 2-1: Surface of catalyst Type (I), Cu_2O. Obtained from C. Ahoba-Sam

2.3.1 Adsorption

For a catalytic reaction, the adsorption of the molecules on the surface of a catalyst is an important part. Adsorption is a surface process, where molecule or particle is bound to the surface of the adsorbent. The adsorption can be weak or strong. Physisorption is a weak adsorption, molecules at the surface feels an attraction between the molecule and the solid caused by Van der Waals force. Strong adsorption is known as chemisorption, where bond in the reactant is broken or weaken, the reactant is bound to the surface of the catalyst. Figure 2-2 show a catalytic reaction for CO oxidation on a metal surface. The cycle starts with molecules diffusion (spread out) through the gas phase to the surface of the catalyst. CO molecules on the surface are adsorbed as an atom because its high bond strength, while O_2 is adsorbed and separated into atoms. In the next step oxygen and CO react together and form CO_2. CO_2 as the product is released, known as desorbed from the surface. Bonds to the surface of the catalyst is broken, and CO_2 enters the gas phase.[11]
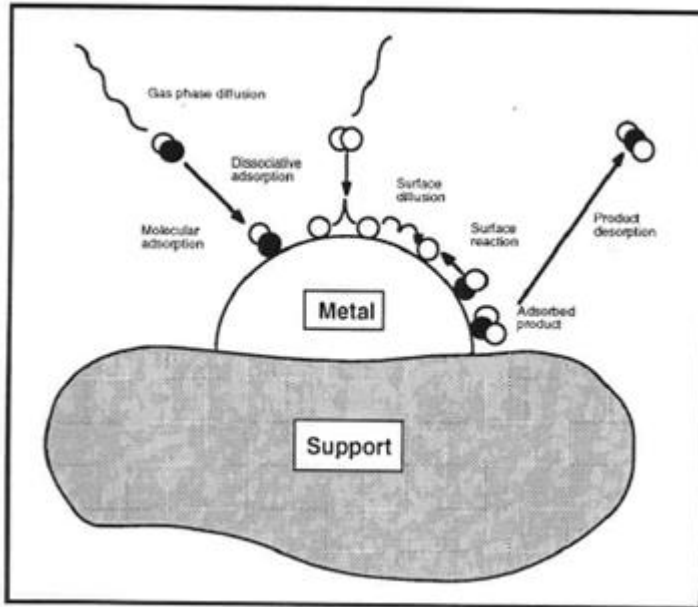
Figure 2-2: Catalytic reaction for CO oxidation on a metal surface [11]

2.3.2   Deactivation

A catalyst will experience a loss in activity with time. Usually, a catalyst goes through a period where it will reach its maximum and then decreases, shown in Figure 2-3. The catalyst has a period at the start where the surface of the catalyst change, in this period steady state in the surface for reactants and product is reached, simultaneous with sintering and segregation. Sintering is separated particles merging and forms a larger particle, result in a smaller surface area for the catalyst. A particle change in size and physical properties is segregation. After a while, the catalyst will reduce the activity, caused by sintering or poison, blocking the active site. [11] The catalyst is poisoned when a compound binds to the active site and makes it unavailable for reaction, the poisoning can be reversible or permanent.[12]
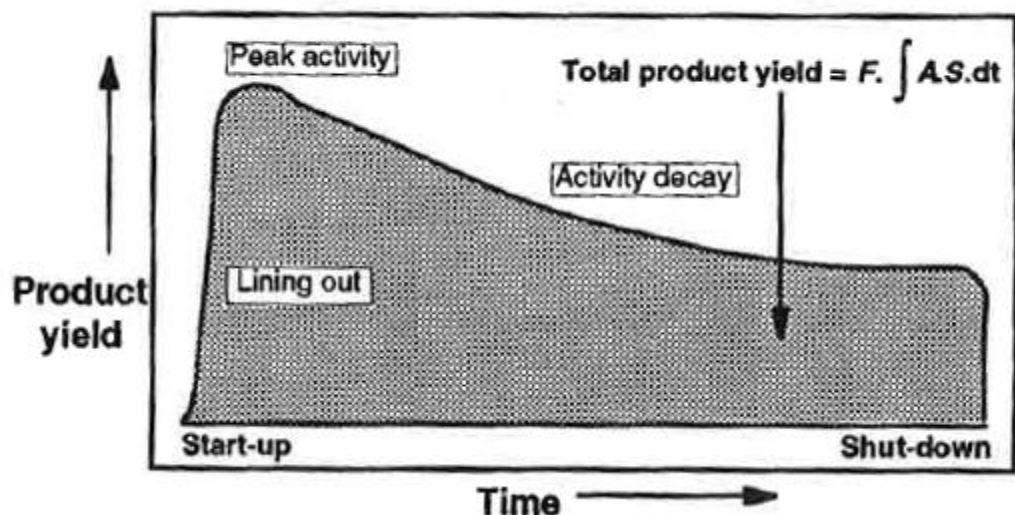
Figure 2-3: Lifetime and product yield of a catalyst.[11]

2.3.3 Temperature dependent

The nature of the catalyst surface can change a lot with respect to temperature, due to this, a reaction may turn around in the reaction rate at a certain temperature.[11]

In the literature, it has been suggested to keep the reaction temperature below 500 K, to avoid CO formation in gas-phase hydrolysis.[2]

2.3.4 Nanoparticle

Over the last years, the focus for nanoparticle has increased due to its potential in a lot of fields, among catalysis.[13] The nano-sized particle has a higher surface area and chemical potential, compared to a larger particle. They often have greater or sometimes new catalytic properties.[6] A decrease in the size of nanoparticles gives an increased surface energy, making the particles react together. Besides the increased surface energy for small particles, the reactivity also depends on the particles size and increase with decreased particle size.[14]

2.3.5 Copper

Copper catalyst has the benefit of being a cheap catalyst with high activity,[15] and is considered to be a good catalyst in hydrolyzing of ester to alcohol.[4]

In the experimental work, air is present in the system at the star of each test. Oxygen removal from synthesis gas by using a copper catalyst has been investigated earlier by Jun

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Han et al.[15]. The copper catalyst can be used in a number of catalytic reaction and was found to be a good oxidation catalyst for removing oxygen from synthetic gas.[15]

2.3.6 Activation method of catalyst

A way to activate a catalyst is to run hydrogen over the catalyst to reduced Cu. For this method, it is difficult to control the rate of reduction. The reaction is exothermic and releases heat. High temperature can cause hot spots on the surface this could cause sintering and loss in activity for the catalyst. After activation, the catalyst should not be exposed to air due to its sensitivity for reoxidation.[7]

2.4 Gas chromatography

Gas chromatography (GC) is a method used in analytic chemistry. This method separates and analyze various compounds in a mixture, based on their retention time. A small volume of gas sample is injected into the inlet of the GC. The carrier gas often helium, transport the sample through the column, where the component of the sample is separated. At the outlet of the column, there is a detector, measure the time and amount of each component leaving the column. [16] Figure 2-3 shows a sketch of a gas chromatograph.
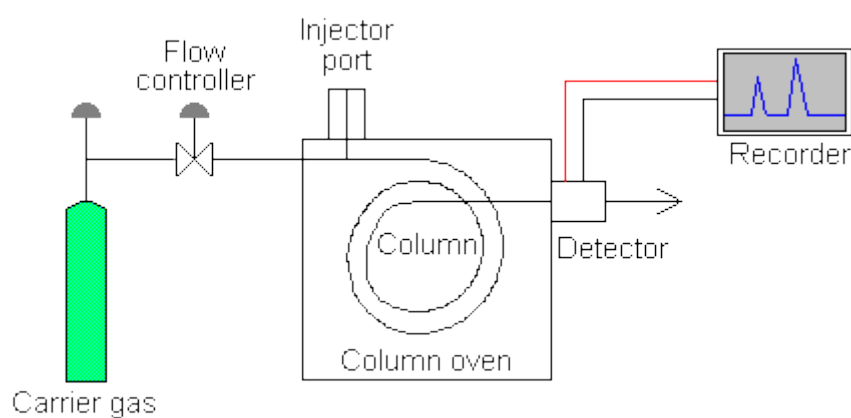
Figure 2-4: Sketch of a gas chromatograph [17]

To ensure stable and desirable temperature for the column, they are placed inside a thermostatic oven. The columns is divided into two types, packed and capillary. The packed column has solid packing as a stationary phase, while the stationary phase in a capillary column is as a layer on their inner walls. [16]

Compounds in the mixture are separated in the column by how strongly they interact with the stationary phase. A strong interaction between compounds and the stationary phase gives long retention time. The separation is mainly based on the boiling point of the compound. A compound with a low boiling point will have a higher vapor pressure, and normally use shorter time through the column compared to a compound with high boiling point. The polarity of compounds will also affect the separation time. Compounds with the same boiling point but different polarity will have different retention time. Generally, ester has lower polarity than alcohol because they are not strongly hydrogen bond. If the column has a non-polar stationary phase, esters who is least polar will use longer time through the column since it interacts more with the stationary phase. Alcohol with higher polarity will have a shorter retention time because of less interaction with the stationary phase. For a polar stationary phase, it will be opposite. [16]

The retention time and the resolution of the peaks varies and are affected by the length of the column, flow rate and column temperature. However, it's not easy to change the length of the column, so other parameters are usually used for adjusting the retention time and improving the resolution. Increasing the column temperature gives a shorter retention time, but it can also reduce the resolution. If a mixture has a large variety in the boiling point, there is no temperature suitable for all the compounds, here temperature programming will be useful. Increasing the flow rate reduce the retention time, but this could also reduce the resolution. The injection heater vaporize the sample quickly this gives more narrow peaks and better resolution. If the injected sample is large, it could also reduce the resolution and give the peaks tailing. Normally the detector is sensitive and doesn't need much material.[16]

2.4.1   Thermal conductive detector

Thermal conductive detector (TCD) is a robust and simple detector with good ability for detecting most component. This detector uses change in the thermal conductivity of the gas stream. The detector has two passages wired to Wheatstone bridge, with an element of metal with high temperature resistance. For the reference cell, the carrier gas will have a constant resistance. The analytic cell will have a change in the resistance with a change in the gas stream. The difference in resistance of the cell gives an output in the form of a peak, where the size depends on the resistance change. The sensitivity depends on the difference between the thermal conductivity of the carrier gas and the component being detected.[16]

3 Literature review

This chapter focuses on earlier research on hydrolysis of methyl formate. Reaction investigated in both gas and liquid phase, over copper-based catalyst. In this work the hydrolysis of methyl formate is in a gas phase, however the reaction and by-product are the same for reaction in both gas and liquid phase. The effect CO and CO_2 has on the hydrolysis of methyl formate is also considered in some of the work.

3.1 Hydrogenolysis of methyl formate over copper-based catalyst

X.Huang et al.[4] studied gas-phase hydrogenolysis of methyl formate at atmospheric pressure over two type copper based catalyst, copper chromite and skeletal copper. The product were analyzed by GCs with TCD, Porapack Q column and CTR-1. Before use the catalyst was reduced, with H_2. In the experiment, there was always stoichiometric or excess of H_2 to methyl formate, the reaction temperature was in the range of 393-453 K. The equilibrium conversion was calculated from different H_2/methyl formate ratio, in the calculation the side reaction was ignored. Calculated equilibrium conversion was in the range of 72-97%, while the experimental conversion was below 18 %. The selectivity to methanol was found to be larger than 95%, with the low conversion condition and CO_2 as the only by-product. The skeletal copper catalyst deactivated fast, this was found to be from fouling caused by polymeric material building up. Copper chromite catalyst did not experience deactivation.

Monti et al.[18] investigated gas-phase hydrogenolysis of methyl formate over silica supported copper catalyst. CO, methyl formate and methanol was separated in a Porapack N column. In the hydrolysis of methyl formate, H_2 was used as a carrier. Hydrolysis of methyl formate at the temperature range of 429-457 K and at partial inlet pressure in the range of 3,5-14,5kPa, the conversion never exceeded 10%. The selectivity for methanol was always above 95%. In their work, they also studied the effect CO has on the hydrolysis of methyl formate for Cu/SiO_2 catalyst. First, the CO/H_2 stream was introduced to the reduced catalyst and a spectrum recorded. A second spectrum was recorded for when methyl formate was added to the CO/H_2 stream and the hydrolysis rate was determined. The third spectrum was made when the CO was shut off and the corresponding hydrolysis rate was measured. They found that the amount of CO adsorbed on the catalyst surface decreased in the presence of methyl formate. CO added to the methyl formate/ H_2 stream

lower the hydrolysis rate without affecting the amount of methyl formate adsorbed on the catalyst surface. Measurement of the heat of adsorption and displacement experiment, indicate that CO was adsorbed less strong on the catalyst surface, compared to methyl formate. They believe that the surface of the copper catalyst will be partially covered by methyl formate molecules, and unoccupied sites are available for H_2. Introducing CO does not displace methyl format, but CO is adsorbed on available sites on the catalyst surface or can displace hydrogen. When CO displace hydrogen on the catalyst surface, it slows down the hydrolysis rate. Another effect from the displacement of hydrogen on the catalyst surface is, partially hydrogenation where among other compounds, formaldehyde can be formed.

Braca et al.[19]investigated the hydrolysis in a gas-phase experiment, using a catalyst of $CuO/ZnO/Al_2O_3$. Gas chromatograph with TCD and flame ionization detector (FID) for analyzing with Porapack QS and Carbosieve column for separation of CO, CO_2 and light hydrocarbon in the product stream. The liquid product analyzed on FID. The test performed at 2,5Mpa in a temperature range of 125- 190°C, their result show that the conversion increased with increased temperature, at 190°C they had a conversion at 80% and selectivity to methanol of 92%. The selectivity to methanol was at 95% at 170 °C with a conversion 66%. At 150°C the conversion was at 36%, and selectivity to methanol at 98%. They varied the pressure in the range of 2.5 to 10MPa, at 125°C, here an increase in pressure showed increased the conversion, while the selectivity to methanol was around 99% at all pressure. They observed a deactivation of the catalyst for long reaction time, assumed to be from the polymerization of formaldehyde.

Sørum[7] investigated hydrolysis of methyl formate in a liquid phase with copper chromite catalyst. He found the hydrolysis of methyl formate to be a true equilibrium reaction, and from a thermodynamical point of view a liquid phase reaction system to have higher conversion than a gas phase. In one experiment, he found the conversion of methyl formate to increase using a catalyst with smaller particle size. He also investigated the effect CO has on the hydrolysis of methyl formate, by adding CO to a standard hydrolysis run, he experienced a drop in the conversion from 65% to 28%. The influence CO_2 on the conversion of methyl formate was also investigated, CO_2 was added in a standard hydrolysis run, the conversion dropped from 65% to 17%. He concluded that CO and CO_2 lower the conversion of methyl formate.

Gormley et al.[20] studied the hydrolysis of methyl formate in a liquid-phase reactor. Raney copper and copper chromite catalyst was compared in a temperature range from 110-160℃. The products stream went to a GC with TCD for analyzing, separated by a Porapack Q column. They saw no sign of deactivation of the catalyst 300 min into the test at 110℃, but at 140℃ and 160℃ there were seen decrease in the rate after 140 to 170 min. There was no good explanation for this drop. In another experiment CO was added, the decrease in conversion was larger. Some CO was formed in all of the experiment, but not enough to cause the total drop in rate. They found that CO inhibits the hydrogenolysis rate of methyl formate over the copper catalyst, less at a higher temperature. At 110℃ the Raney copper catalyst was more active per gram than the copper chromite catalyst at low temperature, at higher temperature the Raney copper catalyst is less active.

Liu et al.[21] studied two-step methanol synthesis in slurry phase, however here is only the part for the hydrogenolysis of methyl formate of interest and revived. Hydrogenolysis of methyl formate was carried out in a batch reactor, before testing the reactor was flushed with H_2 to remove air. The test was performed in a temperature range of 100°C-140°C, where the pressure was kept constant by adding H_2 continuously. For the hydrolysis copper chromite catalyst was used, this was reduced under H_2 atmosphere at 170℃. The hydrogenolysis was found to be very selective to methanol, and no detection of by-product with GC analyze. The study concludes with that the hydrogenolysis rate can be increased by using higher reaction temperature. The effect CO has on the hydrolysis rate was also studied, the damaging effect from CO was found to be partially reversible when CO was removed. Deactivation of the catalyst due to CO can be a potential problem. The effect of CO_2 on the hydrolysis of methyl formate was also studied. CO_2 was added to the reactor in the gas phase, a reduction in rate was seen from this. CO_2 was removed by cooling down the reactor to 22℃ and removing 90% of the gas phase. The reactor was after this heated to 130℃ and pressurized with H_2. After CO_2 was removed the hydrolysis rate was lower, compared to the hydrolysis rate before CO_2 was added. CO_2 This indicates that CO_2 can poison the catalyst.

Li and Jens[22] reported a new low-temperature methanol synthesis (LTMS) catalyst system, produced by the reaction of $Cu(CH_3COO)_2$, NaH and methanol. They investigated the methanol synthesis in two steps, there experiment were performed in a batch reactor in a temperature range of 80-120°C and pressure range for 10-20 bar. For both reactions, syngas to methyl formate and methyl formate to methanol were both accelerated by pressure and temperature increase. They concluded that methanol synthesis in one step gives a higher formation of methanol product compared to the two step.

4 Method

The test rig was located at USN. The experimental process attached on the rig was modified and equipment calibrated before the experimental work started. In this chapter is the process described along with calibration data, catalyst specification and experimental setup.

4.1 Process description

The process used for the testing is on a rig, located in the HPLC laboratory and illustrated in Figure 4-1. Valves who can be operated manual has HV as an abbreviation for hand valve next to them in the figure. N_2 and H_2 enter the system through each mass flow controller (MFC). N_2 enters the glass bottle filled with methyl formate, and flows through a plastic tubing inside the glass bottle with an entrance below the liquid level of methyl formate. In this way, nitrogen bubbles through the methyl formate and carries it to the reactor. To keep methyl formate in vapor form the lines are heated and insulated. H_2 and methyl formate meets in the line before they enter the reactor. The reactor is heated by an oven. The product stream out of the reactor can be sent either to waste or to a GC for analysis.

Process diagram
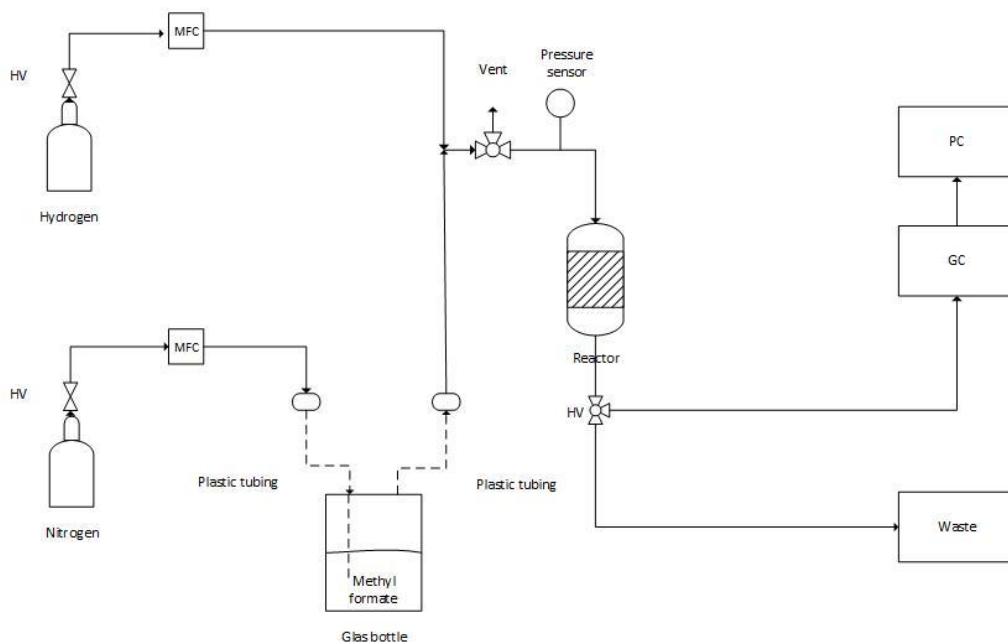
Figure 4-1: Process diagram of the test rig.

A labwiev program controls the MFC, shut down valve and the oven, while a separate controller controls the heating of the pipe.

4.1.1 Leak checking the rig

All connections on the test rig are a potential source of leaking. The test rig were systematically leak checked before the experiment started. This was done part by part, by looking at pressure drop, using soap water for the connection and using a gas detector. Leak check was done by pressurizing the system to about 3 bars while the end of the reactor was blocked for 20 min to check for any drop in pressure.

4.1.2 Leak problem

The glass bottle and its tubing connected to the steel was a major source of a leak for a long time. A number of different tubing with connection were tested, first the problem seemed to be in the connection to the steel. When this problem was solved, a new appeared. The connection between round bottle flask and the glass pipe inside was difficult to get leak thigh, for a pressure above 0.7 bar. In order to solve this problem, the glass bottle was replaced with one that had a screw cap. The tubing inside the bottle was

attached with screw connection. Two plastic line connected the screw cap to the rest of the system. This system showed no sign of leak when tested according to the rest of the system.

4.2 Temperature control

The temperature was controlled for the reactor and the piping.

Temperature control of the reactor:

An oven with a height of 11 cm surrounds the middle part of the reactor, illustrated in Figure 4-2. The oven temperature is measured by an internal thermocouple in the oven. Before the experiment, the temperature inside the reactor wall was measured manual by a thermometer, with known temperature and set point of the oven.
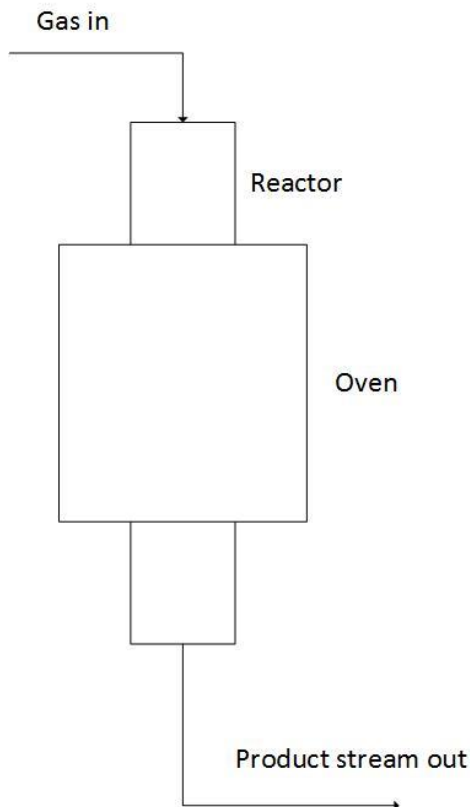
Figure 4-2: Sketch of the oven surrounding the reactor.

Figure 4-3 gives the relation between temperature in the oven and the temperature inside the reactor wall, according to the length of the reactor covered by the oven. The figure shows that the warmest place is in the middle of the oven, measured at the length, 6cm. Values for the temperature measurement is in Appendix 3.
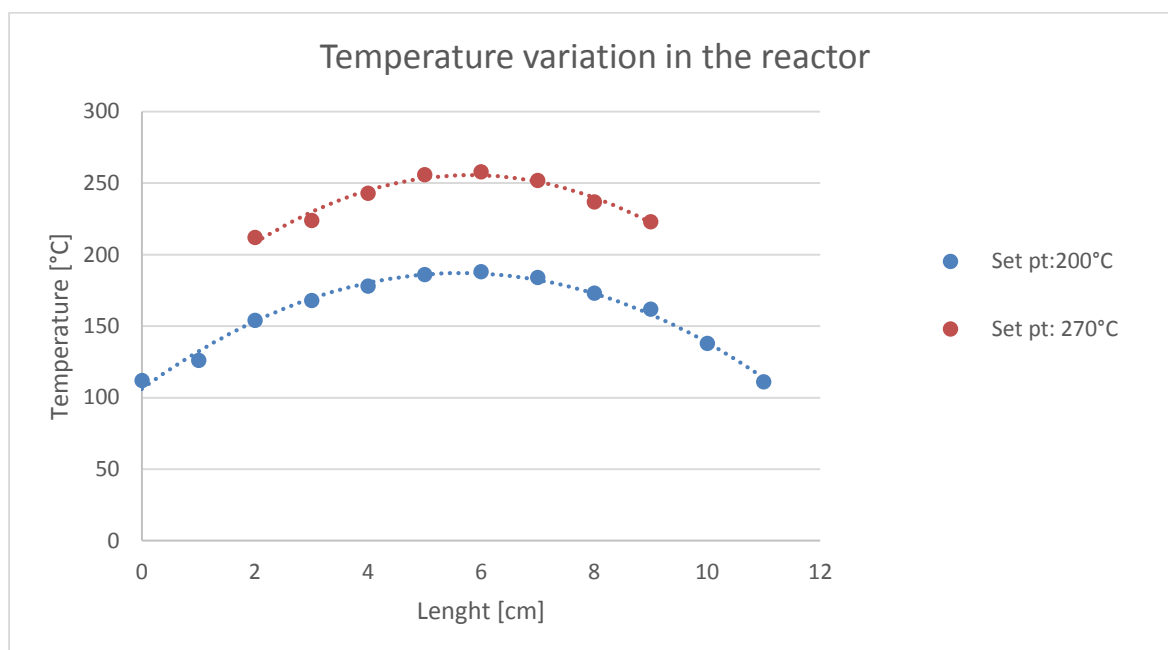
Figure 4-3: Temperature inside the reactor measured manual compared to set point and temperature of the oven.

Heating the lines:

To avoid methyl formate to condensate in the pipe, the piping from the methyl formate bottle to the reactor was heat traced and insulated. The lines from the reactor to the GC was also heat traced and insulated, to avoid compensating the product, mainly methanol, unreacted methyl formate and other possible heavy products. The set point of the heated line was 100°C.

4.3 Measurement of the gas

The process was run in a labwiev program, controlling gas in through mass flow controller (MFC) and the heat of the oven. The program also had a pressure indicator placed before the reactor, and a three-way valve to switch between into the reactor and ventilation.

 Mass flow controller (MFC):

The MFC controlling the flow into the system where used for hydrogen and nitrogen. Earlier the MFC used for H_2 had been calibrated for H_2, while the one used for N_2 had been calibrated for helium. The MFC used for N_2 was checked with N_2 flow against a flowmeter for deviation in the flow. Figure (4-4) shows the values for the digital and manual flow measurement, data the figure is based on is in Appendix 4.
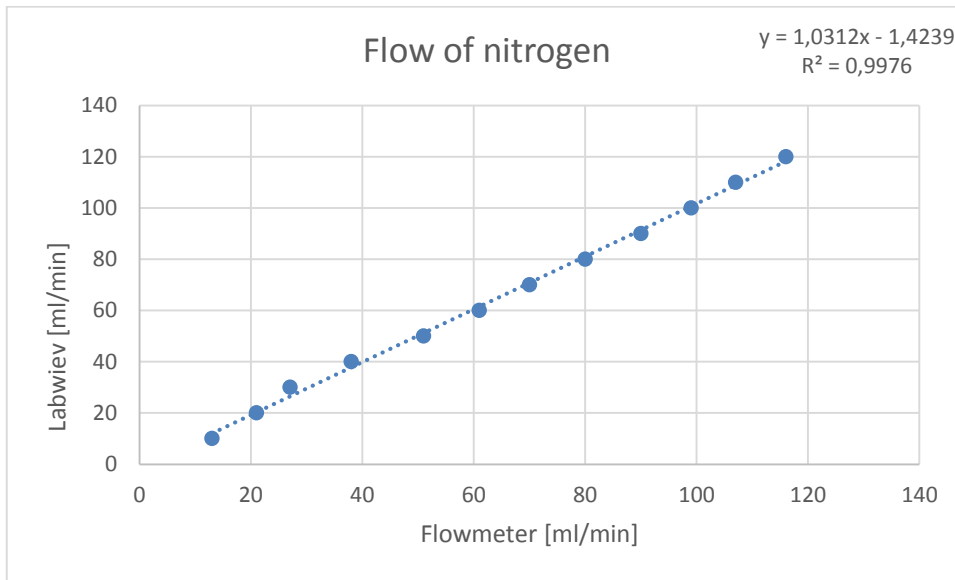
Figure 4-4: Calibration curve for MFC of nitrogen

In equation (4-1) the wanted flow of N_2 is F and $F_{N_2,sp}$ is the inserted set point to the labwiev program to achieve this flow.

$$F_{N_2,sp} = 1,0312 \cdot F - 1,4239 \tag{4-1}$$

Pressure measurement:

The digital pressure measurement were calibrated against a manual pressure manometer, the measurement some deviation. The relation between the pressure measurements is illustrated in Figure (4-5) and the data the figure is made of is in Appendix 5.
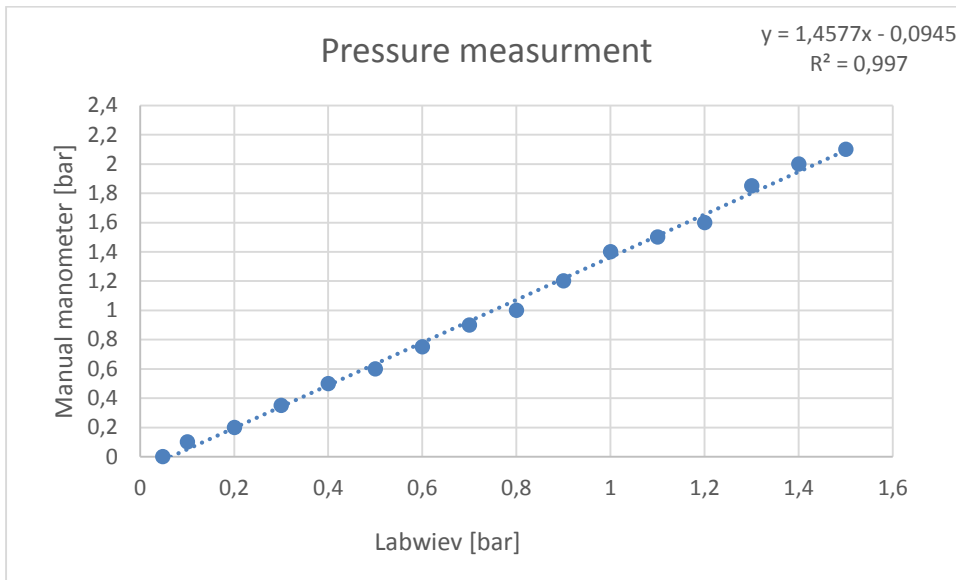
Figure 4-5: Calibration of pressure measurement.

The pressure of the system is given by linear curve fitting and gives the pressure in equation (4-2).

$$P = 1,4577 * P_{Labwiev} - 0,0945 \qquad\qquad (4-2)$$

4.3.1 Vapor pressure of methyl formate

The vapor pressure with respect to temperature was found for methyl formate with data obtained from NIST[23],the values used is listed in Appendix 6, Figure 4-6 was made from this values.
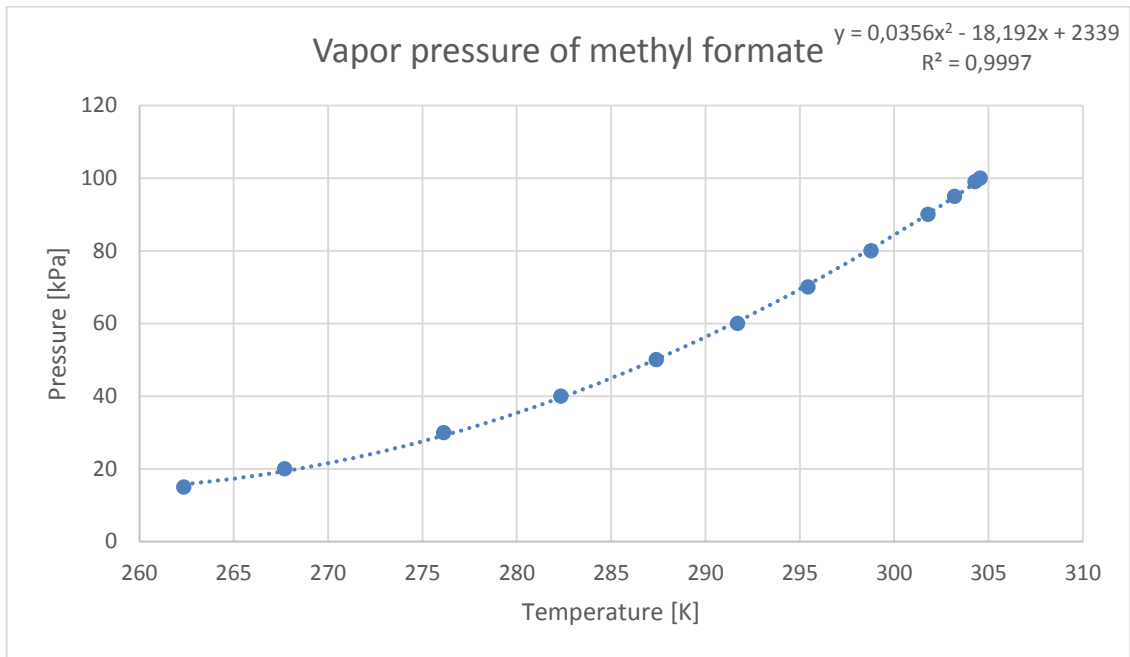
Figure 4-6: Vapor pressure of methyl formate.

From the figure a polynomial curve fitting was done, this gives equation (4-3).

$$p_{MF}^{\circ} = 0{,}0356T^2 - 18{,}192T + 2339 \qquad (4\text{-}3)$$

4.3.2 Vapor pressure of methanol

The vapor pressure with respect to the temperature are obtained from NIST[24], values used is given in Appendix 6. From this data, Figure 4-7 was made.
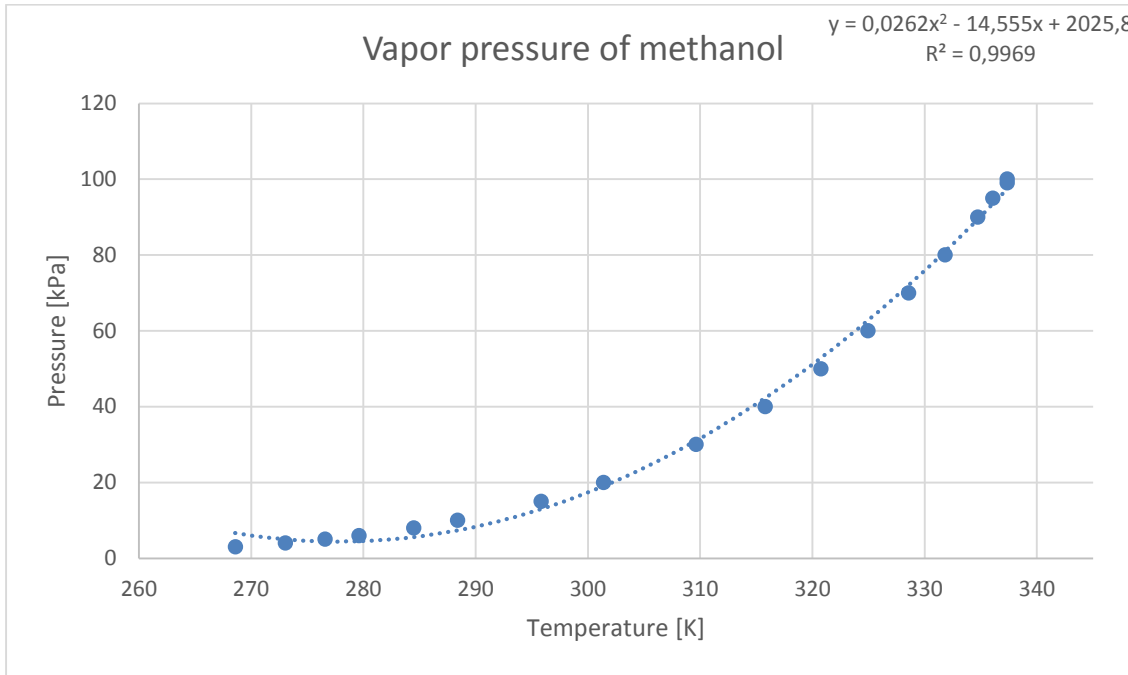
Figure 4-7: Vapor pressure of methanol.

From the figure a polynomial curve fitting was done, this gives equation (4-4).

$$p^{\circ}_{MeOH} = 0,0262T^2 - 14,555T + 2025,8 \tag{4-4}$$

4.4 Gas phase reaction

The experimental reaction, (R1-2) and elementary reaction (R4-1)

$$. HCOOCH_3(g) + 2H_2(g) \leftrightarrow 2CH_3OH(g) \tag{R1-2}$$

$$A + 2B \leftrightarrow 2C \tag{R4-1}$$
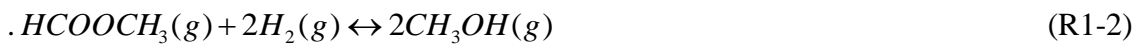
A general mole balance is given in equation (4-5). Assuming the reactors a continuous stirred-tank reactor (CSTR). The general mole balance for CSTR reactor in equation (4-6) Where F_{AO} is the molar flow of A in, and F_A is the molar flow of A out. The rate of formation of A is r_A, V the volume and Na the number of moles of A inside the system.[25]

$$IN - OUT + GENERATION = ACCUMULATION \tag{4-5}$$

$$F_{AO} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt} \tag{4-6}$$

Assuming steady state and well mixed gives equation (4-7).

$$F_{AO} - F_A + r_A V = 0 \tag{4-7}$$

4.5 Catalyst

Two types of copper catalyst nanoparticles was used in the testing, both obtained from C. Ahoba-Sam.

- Type (I): Copper (I) consisting of Cu_2O with a crystallite size 15,9 nm and a particle size of 25nm.
- Type (II): Copper (II) consisting of CuO with a crystallite size 4,5 nm and a particle size of 21nm.

Analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM)

Figure 4-8 show the particle and crystallite for catalyst Type (II). XRD graph and TEM images of catalyst Type (I) and Type (II) obtained from C. Ahoba-Sam in Appendix 8.
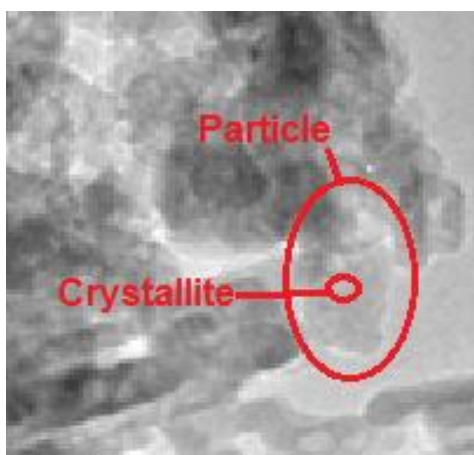
Figure 4-8: Particle and crystallite for catalyst Type (II).

The reactor was packed to middle height, 12.5 cm, with wool, where the catalyst was placed on top. The catalyst was used as given and activated according to the activation procedure for the catalyst.

4.5.1 Activation of the catalyst

The catalyst was activated in the reactor by flowing 20ml/min H_2 over the catalyst at 250°C for 2 hour Reaction procedure/ experimental setup

4.5.2 Catalyst performance

The conversion of methyl formate was calculated from the concentration of the carbon components in the product stream, equation (4-8). The equation is based on the assumption

that these are the only carbon components in the product stream. [4] The concentration is given as Y the mole% for methanol (Y_{CH_3OH}), methyl formate (Y_{HCOOCH_3}), CO (Y_{CO}) and CO_2 (Y_{CO_2}).

$$Conversion(\%) = \frac{Y_{CH_3OH} + Y_{CO} + Y_{CO_2}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-8}$$

The selectivity was also calculated from the concentration of components in the product stream, under the same assumption as for equation (4-8), of methanol, methyl formate, CO and CO_2 being the only carbon components in the product stream. The selectivity for methanol can be calculated from equation (4-9), selectivity to CO from equation (4-10) and selectivity to CO_2 from equation (4-11) where Y is the mole% of each component. [26]

$$Selectivity_{MeOH} = \frac{Y_{CH_3OH}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-9}$$

$$Selectivity_{CO} = \frac{Y_{CO}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-10}$$

$$Selectivity_{CO_2} = \frac{Y_{CO_2}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-11}$$

4.6 Experimental setup

The experiment where performed at a pressure of 0,9 bar, with 200mg catalyst and a total flow rate of 100ml/min into the reactor. The ratio of H_2/Methyl formate ratio was 2.3, calculated from partial pressure of H_2 and methyl formate. The distribution of the various component in the flow is listed in Table 4-1. The flow of methyl formate into the reactor is a calculated value, calculated from partial pressure. Properties of the reactor, calculation of the H_2/methyl formate ratio and the flow of methyl formate into the reactor in Appendix 7.

100 ml of methyl formate was put in a glass bottle with a volume of 500 ml before each experiment. The glass bottle was placed in a container filled with ice, the ice was changed in intervals of 3-4 hour to maintain the temperature of 0 °C for methyl formate. Increasing the temperature would give an increase in vapor pressure for methyl formate, which may lead to faster flow rate than expected.

For the analyze of the product stream a test was taken every 13 min, the process was run in steady state.

Table 4-1: The flow and purity of the components into the reactor.

Component	Flow	Purity
MF	15,5 ml/min (calculated)	99,00%
H_2	35,0 ml/min	100%
N_2	49,5 ml/min	99,99%

After an ended experiment, the reactor temperature was reduced to 22°C. The glass bottle with methyl formate was removed and the system was purged with 50ml/min N_2 for 10 minutes, to quickly remove the reactants in the reactor and stop the reaction. Further, the system was purged with 20ml/min N_2 for 40 min, to remove all carbon compound in the system.

The space velocity (SV) was calculated from equation (4-12), where V_o is the total volume flow rate into the reactor and m_{cat} the mass of the catalyst used in the experiment.[27]

$$SV = \frac{V_o}{m_{cat}} \ (m^3 kg^{-1} s^{-1}) \tag{4-12}$$

SV is $0,083 m^3 kg^{-1} s^{-1}$, all values in the calculation are given in Appendix 7.

4.7 Calibration of gas chromatograph

Agilent 7890 A, gas chromatograph (GC) was used for analyzing containing Porapack Q, Molecular Sieve and Haye Sep Q column. Specification of the column is given in table 4-2. The carrier gas used is helium.

Table 4-2: Specification of the column in the GC.

Column	Mesh	Length	Outer diameter	Material
Porapack Q	80/100	9 Ft	1/8 in	Stainless steel
Molecular Sieve	60/80	6 Ft	1/8 in	Stainless steel
Haye Sep Q	80/100	3 Ft	1/8 in	Nikkel

The GC has one inlet, and the Porapack Q and the Molecular Sieve are in series, with Haye Sep Q column for backflushing. Separation of H_2, N_2 and CO in the Molecular Sieve column, while CO_2, methanol and methyl formate was separated in the Porapack Q column. The Porapack Q can be used for separation of methanol[28] and methyl formate[29]. The outlet of the GC goes to a thermal conductive detector (TCD).

4.7.1 Method for analyzing the product stream

A method to analyze the product stream on the GC was first made. The column is in series, the stream was backflushed, when CO_2, methanol, and methyl formate left the Porapack Q column, to avoid blocking pores in the Molecular Sieve column. The time for the backflush needed to be "timed" in order for detection of all components. The product mix has a large variety in boiling point, this made the program making for the analysis some challenging. Since the separation compound is based on the difference in boiling point. Isothermal temperature for the oven was not satisfying and temperature programming was adopted.

The method for the analyses of the product stream in Appendix 9.

4.7.2 Calibration of the GC

The calibration was done with calibration gas containing CO, CO_2, N_2 and H_2, methanol and methyl formate. Each molecules retention time was identified. H_2 has higher thermal conductivity than the carrier gas helium, [30] and appear as a negative peak. A program integrated all peaks, also negative peaks, giving consistent analyze of the peaks for where the data was cut off and the distance to the baseline.

The concentration of methyl formate and methanol was calculated from vapor pressure from equation (4-3) and (4-4) and the total pressure, small variation showed to have a large impact on the concentration. For the calibration, the average of three points with the same

condition was used for calculating the response factor, calibration data use is listed in Appendix 10.

Figure 4-9 show an analyze of the product stream, starts from left with H_2, CO_2, methanol, methyl formate, N_2 and CO.
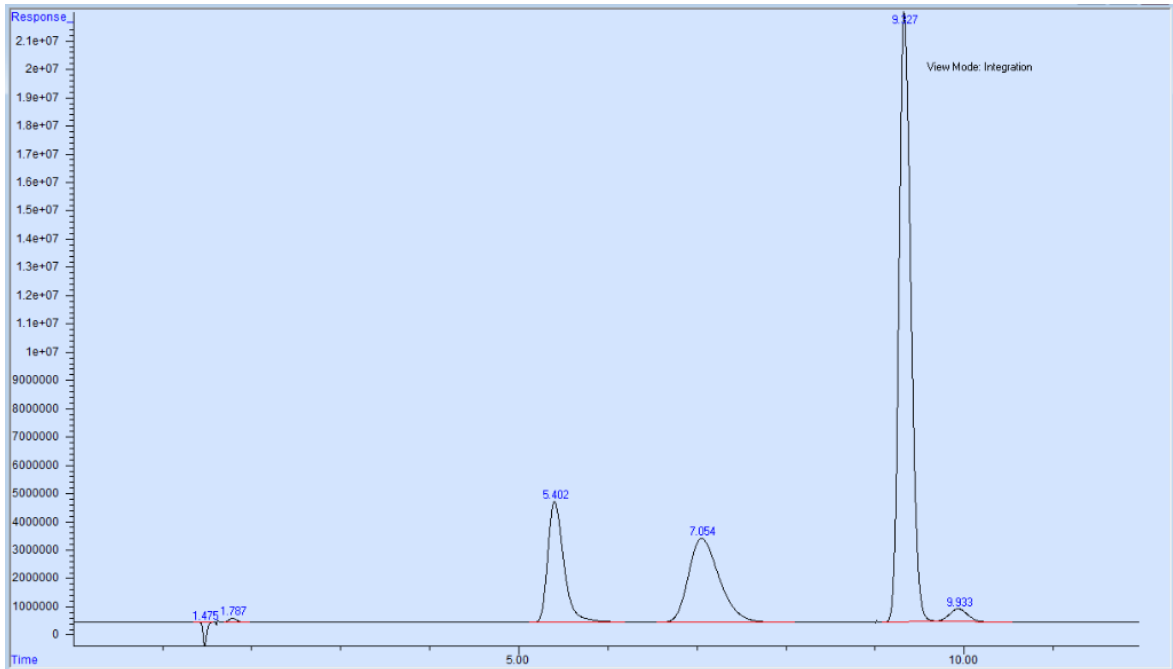
Figure 4-9: Analyze of the product stream, from left: H_2, CO_2, methanol, methyl formate, N_2 and CO.

4.8 Health, safety and environment

In the laboratory, there are numerous hazard gasses and chemicals. For the experimental work in the laboratory, it is important to be aware of potential hazard and safety measure. A safe job analyzes (SJA) was performed before the work started, this is given in Appendix 2. The process has valves for closing in case of emergency.

5 Results

In this chapter is the result of the experimental work. Catalyst Type (I) was tested at 170°C, 210°C and 250°C with an extended test at 250°C. Catalyst Type (II) was tested at 250°C. Initially catalyst Type (I) was tested at 160°C, but there was no indication of reaction after on hour, and test was stopped.

Conversion, selectivity to methanol, CO and CO_2, and mole% H_2 in the product stream is graphically illustrated.

In the testing, the flow into the reactor is:

- 35 ml/min H_2 (100%)
- 15,5 ml/min Methyl formate (99%), calculated value
- 49,5ml/min N_2 (99.99%)

The catalyst used in the testing is a copper catalyst and defined as follows:

- Type (I) consisting of Cu_2O with a crystallite size 15.9 nm and a particle size of 25nm.
- Type (II) consisting of mostly CuO with a crystallite 4.5 nm and a particle size of 21nm.

Analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The catalyst was activated before each test, according to the activation procedure, where H_2 was flown over the catalyst for one hour at 250°C. The amount of catalyst used was the same in all test, 200mg.

For the test, methyl formate in liquid form was placed in a glass bottle connected with tubes to the system. This glass bottle was placed in an ice bath, to maintain a temperature 0°C for methyl formate. The ice was shifted in intervals of 3-4hour, to avoid a temperature increase of methyl formate when the ice melted.

The reaction temperature for catalyst Type (I) is 170°C, 210°C and 250°C, and catalyst Type (II) is 250°.

The reaction for the hydrogenation of methyl formate normally gives methanol as the main product and has CO and CO_2 as the most common by-product. At the start of a test, there is

air in the system, where O_2 probably lower the effect of the hydrolysis of methyl formate in the start.

Reaction (R5-1) the main reaction, hydrolysis of methyl formate to methanol.

$$HCOOCH_3 + 2H_2 \leftrightarrow 2CH_3OH \tag{R1-2}$$

Reaction (R2-1), (R2-2) and (R2-4) are reaction where only methyl formate reacts.

$$HCOOCH_3 \rightarrow CO + CH_3OH \tag{R2-1}$$

$$HCOOCH_3 \rightarrow CO_2 + CH_4 \tag{R2-2}$$

$$HCOOCH_3 \rightarrow 2CH_2O \tag{R2-4}$$

Hydrolysis of methyl formate to methanol and formaldehyde, in reaction (R2-6).

$$HCOOCH_3 + H_2 \rightarrow CH_2O + CH_3OH \tag{R2-6}$$

Formaldehyde reacts further in reaction (R2-7)

$$CH_2O \rightarrow CO + H_2 \tag{R2-7}$$

Reaction (R5-4) oxidation of CO.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{R5-1}$$

The calculation for the conversion and selectivity is calculated from carbon atoms in the product stream, Y is the mole% of each component. The calculation assumes that methanol, methyl formate, CO and CO_2 are the only carbon-based product in the product stream. The conversion is calculated according to equation (4-8).

$$Conversion(\%) = \frac{Y_{CH_3OH} + Y_{CO} + Y_{CO_2}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-8}$$

The selectivity for methanol calculated from equation (4-9), CO from equation (4-10) and CO_2 from equation (4-11).

$$Selectivity_{MeOH} = \frac{Y_{CH_3OH}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-9}$$

$$Selectivity_{CO} = \frac{Y_{CO}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-10}$$

$$Selectivity_{CO_2} = \frac{Y_{CO_2}}{Y_{CH_3OH} + Y_{CO} + Y_{CO_2} + 2 \cdot Y_{HCOOCH_3}} \cdot 100\% \tag{4-11}$$

5.1 The effect of temperature on catalyst Type (I)

Figure 5-1 shows the conversion for catalyst Type (I) 1. Tested, at 170°C, 210°C and 250°C versus time. The curve for conversion for catalyst Type (I) at 170°C has shorter timeline than the other test. This because the ice in the bath methyl formate was placed melted, the temperature of the methyl formate increased and hence the flow rate of methyl formate into the reactor. Increased amount of methyl formate into the reactor change the ratio between methyl formate and H_2 since the concentration of H_2 is the same. This gives an increased amount of methyl formate in the product stream and a reduction in calculated conversion. Catalyst Type (I) at 250°C at the start of the test has a decrease in the conversion before increase again. This is because mole% methyl formate in the product stream increase before it decrease again. The decrease in conversion with time at 250°C, could be caused by sintering.

Catalyst Type (I) at 210°C has stable conversion e with time and do not show the same loss in conversion, seen at temperature 250°C.

The figure shows that the highest conversion is at 250°C, where the highest measured conversion is 67%. At 210°C, the highest measured conversion is 31% and at 170°C the highest measured conversion is 29%. Data for Figure 5-1 in Appendix 11.
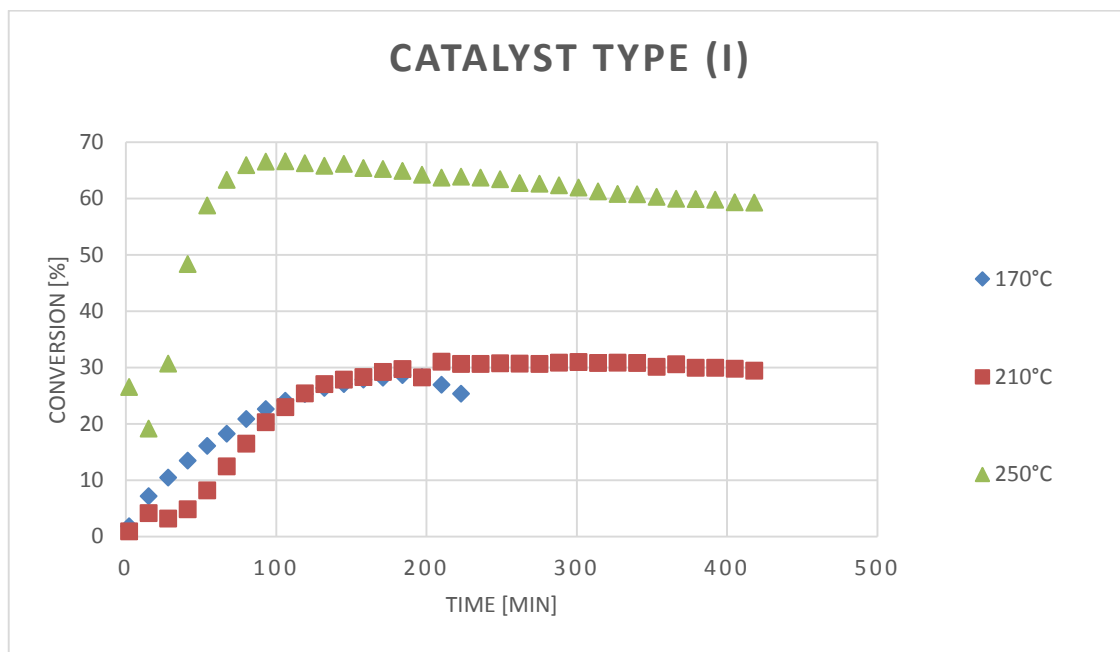
Figure 5-1: Conversion for catalyst Type (I) 1. Tested, at 170°C, 210°C and 250°C, versus time.

5.2 Catalyst Type (I) and Type (II) at 250°C

Figure 5-2 show the conversion versus time graph for the catalyst Type (I) and Type (II) at 250°C. At the beginning of the test, catalyst Type (II) has a smaller drop in conversion compared to catalyst Type (II). The conversion is highest for catalyst Type (II), who has smaller crystallite size and particle size than catalyst Type (I). In addition to the difference in crystallite and particle size the catalyst has some difference in composition. The conversion for both catalysts show the same decrease with time, this could be caused by sintering. The increase in one point for conversion curve catalyst Type (II) after 300 min is a result of measurement error. Values for Figure 5-2 in Appendix 12.
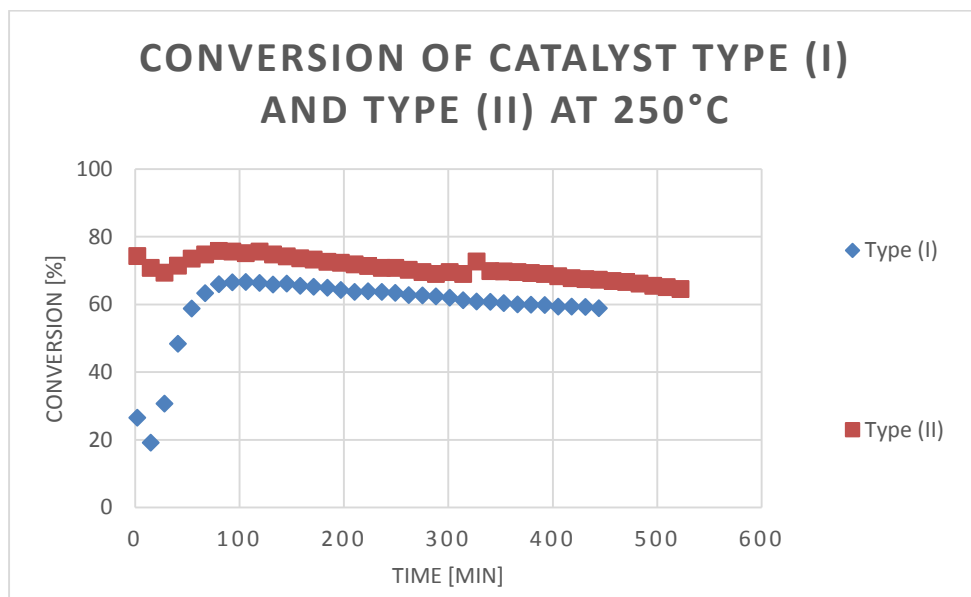
Figure 5-2: Conversion for catalyst Type (I) and Type (II) over time, at 250°C.

5.3 Catalyst Type (I) tested over 2 day at 250°C

Catalyst Type (I) was tested over 2 days period at 250°C. Since methyl formate was kept in an ice bath during the experiment as explained earlier, the ice needed to be shifted in interval. Between the days, the system was parked with closed valves at each side of the reactor, the reactor was pressurized to 3 bar before closing and the temperature reduced to 80°C. The system was started up the next day with the same condition for flow, temperature and pressure as the day before.

Figure 5-3 show conversion versus time graph for catalyst Type (I) at 250°C, where data from both days are reported continuously. The first day the catalyst had the highest conversion of 67% after 106 min, the conversion decreased after 39 min. At the end of the day 1, after min 444 the conversion was 59%. The second day, the catalyst had the highest measured conversion of 52% after 563 min, the conversion decreased after 39 min, when the system was stopped after 953 min the conversion had decreased to 45%. Data for Figure 5-3 in Appendix 17.
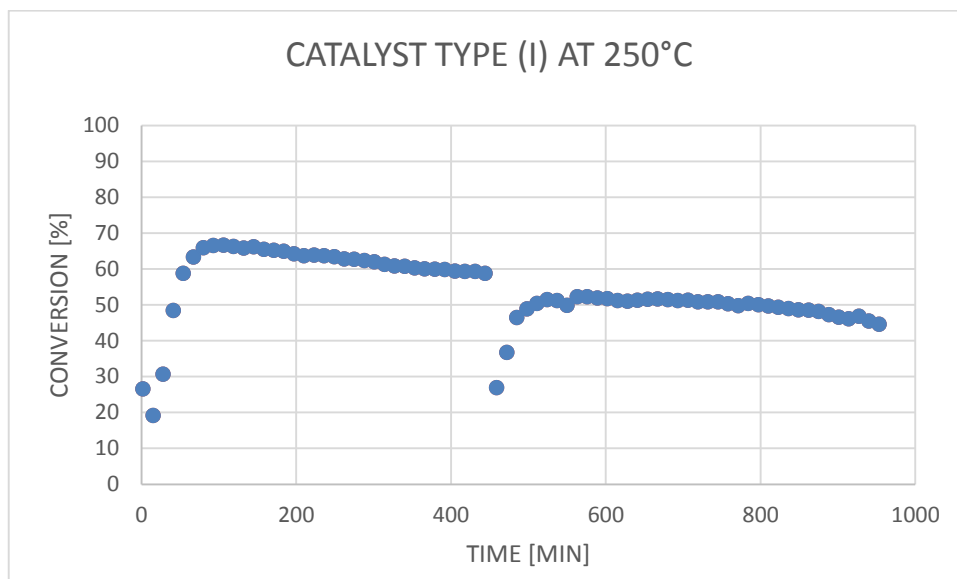
Figure 5-3: Conversion for catalyst Type (I) at 250°C tested over 2 days

The test of catalyst Type (I) at 250°C was initially tested over three days. Data from the third day showed an unexplainable increase in the conversion the third day, and are not included in the result. The figure from all three days is included in Appendix 17.

Catalyst Type (II) at 250°C was initially tested over two days. The testing was preformed in the same way as for catalyst Type (I) at 250°C. Data from the second day showed an unexplainable increase in conversion and its not included in the result. Data for the test and the figure of conversion versus time is in Appendix 18.

5.4 Reactivation for catalyst Type (I)

The catalyst Type (I) was reactivated 2 times, after the first test at 170°C, 210°C and 250°C. The criterion for reactivating the catalyst was that the conversion went below 5%. This criterion was followed, but after the testing, it was discovered that the low conversion was a result of a high flow of methyl formate into the reactor. The high flow of methyl formate was a result of the ice melting in the ice bath, increasing the temperature of the methyl formate and hence the flow rate. The catalyst was activated before each test according to the activation procedure.

Figure 5-4 show the conversion versus time graph at 170°C for catalyst Type (I). At this temperature, the catalyst is tested for a shorter time compared to the test at a higher temperature. This is because of increased amount of methyl formate into the reactor, from

ice melting in the ice bath, as explained earlier. This leads to a decrease in the calculated conversion. The curve for the catalyst first time tested is short and affected of this. The other activity for the catalyst, second and third with reactivation in between also show the effect of increased amount of methyl formate into the reactor.

The conversion was 21% at time 106 min, and then increased to 29% after 197min, the conversion decreased after 26 min.

A second and third activity of the catalyst after reactivation in between of each. The highest measured conversion, which was 29% after 197 min in the first case, was 22% and 15% in the second and third case respectively. Data for Figure 5-4 in Appendix 13.
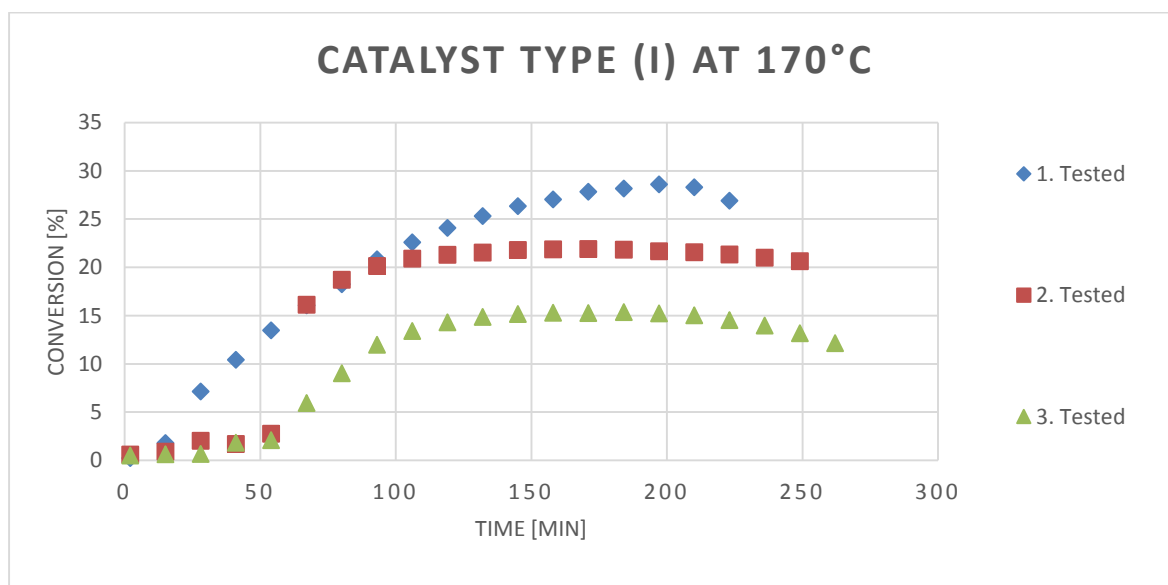
Figure 5-4: Conversion of catalyst Type (I), 1.Tested, 2.Tested and 3.Tested, with reactivation of the catalyst between each test, at 170°C.

Figure 5-5 shows the conversion versus time at 210**°C** for catalyst Type (I). The decrease in the conversion at the start for the catalyst first time tested, is a result of the mole% methyl formate the product stream, increase before it decreases. The mole% methanol in the product stream is increasing from the beginning of the test. After 200 min the conversion for the catalyst has a decrease in conversion, this is a result of measurement errors. The third activity measured after two reactivation of the catalyst, has a decrease in the conversion with time, this could be from sintering.

Conversion was 23% at time 106 min, and then increased to 31% after 301 min, the conversion decrease after 169 min.

A second and third activity of the catalyst was tested after reactivation in between each. The highest measured conversion, which was 31% after 301 min in the first case, was 25% and 24% in the second and third cases respectively. Data for Figure 5-5 in Appendix 14.
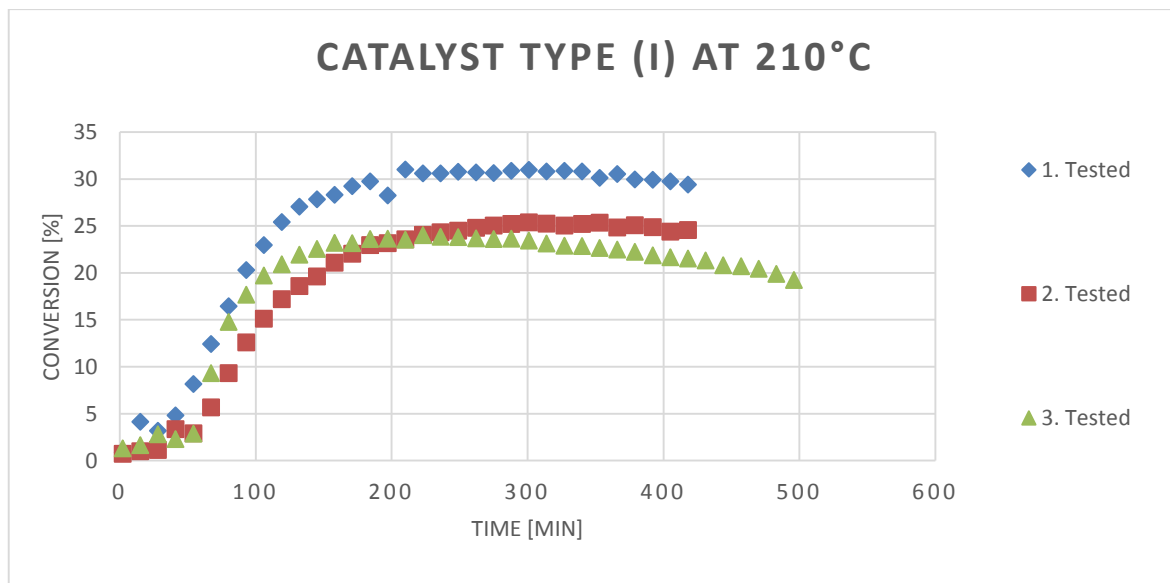

Figure 5-5: Conversion of catalyst Type (I), 1.Tested, 2.Tested and 3.Tested, with reactivation of the catalyst between each test, at 210°C.

Figure 5-6 shows conversion versus time graph at 250°C for catalyst Type (I). At the start of the test the conversion decrease before it increase. This caused by the mole% methyl formate in the product stream. The mole% methanol in the product stream increasing from the start without decrease. The conversion at all of this temperature show a decreasing in conversion with time, this can be an effect of sintering of the catalyst.

The conversion was 31% after 29 min, and then increased to 67% after 107 min, the conversion decreased after 39 min.

A second and third activity of the catalyst was tested after reactivation in between each. The highest measured conversion, which was 67% after 107 min in the first case, was 61% and 58% in the second and third cases respectively. Data for Figure 5-6 in Appendix 15.
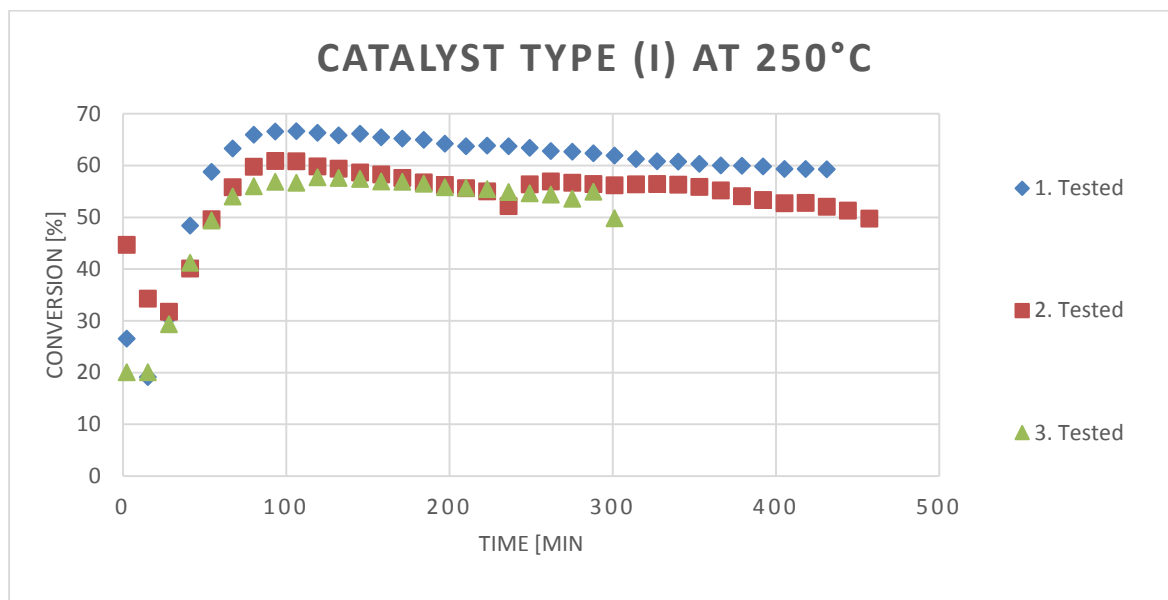
Figure 5-6: Conversion of catalyst Type (I), 1.Tested, 2.Tested and 3.Tested, with reactivation of the catalyst between each test, at 250°C.

5.5 Highest conversion with time

Figure 5-7 shows the highest measured conversion and the time before it starts decreasing. The figure shows that catalyst Type (II) at 250°C has the highest measured conversion, but after 52 min the conversion starts reducing. For catalyst Type (I), the highest measured conversion is at 250°C. At this temperature, the conversion starts reducing after 39 min for all the teste. Test of catalyst Type (I) at 210°C has for the catalyst first- time tested a decrease in the conversion after 169 min. At this temperature the time for before the conversion starts decreasing is lower each time the catalyst is tested, with reactivation in between of each test. At 170°C, catalyst Type (I) shows a decrease in the conversion after a short time. The ice melting, and further temperature increase for methyl formate, as explained earlier cause the decrease in conversion. Data for Figure 5-7 in Appendix 19.
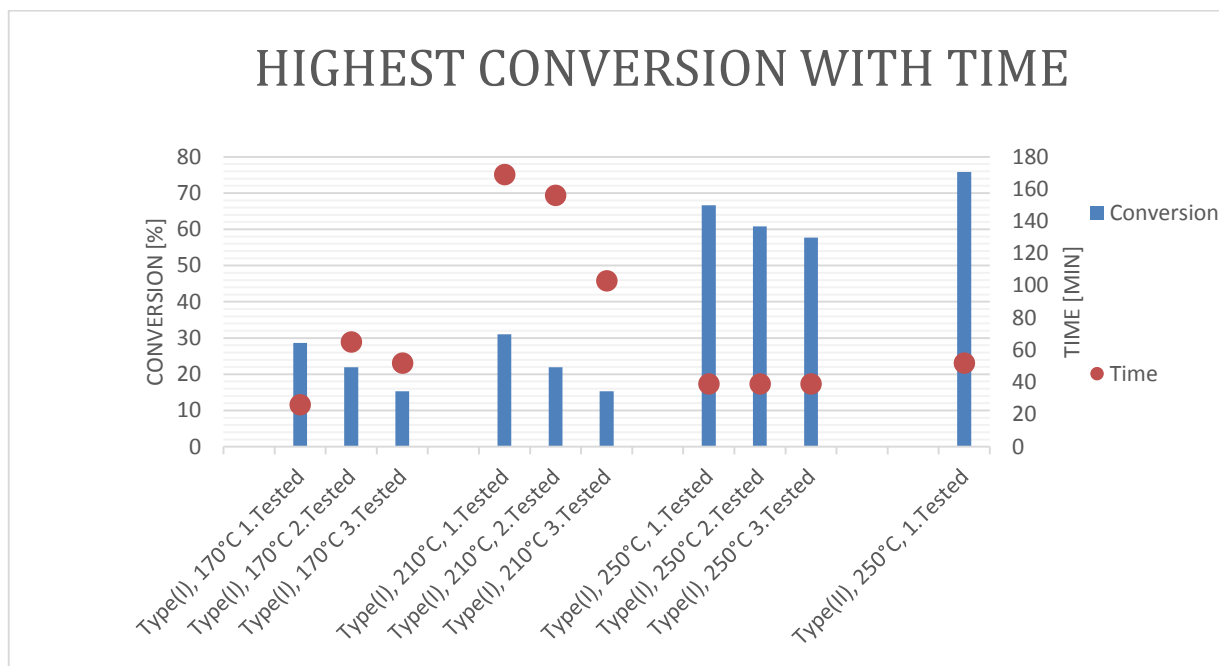
*Figure 5-7: Catalyst Type (I) tested at 170°C, 210°C and 250°C, with reactivation of the catalyst between each test on each temperature. Catalyst Type (II) tested at 250°C. Time before catalyst has decrease in conversion.*

5.6 Selectivity

The selectivity to methanol, CO and CO_2, was calculated from the concentration of carbon-based atoms in the product stream. The selectivity graph is made with data from the catalyst first time tested at each temperature, mole% H_2 in the product stream and conversion is also included in the graph. In the start of a test, there is air in the system and this interferes with the hydrolysis reaction.

Figure 5-8 shows conversion and selectivity to methanol, CO and CO_2, and mole% H_2 in the product stream, for catalyst Type (I) at 170**°C**, with time. In the start of the test, O_2 is in the system. The selectivity to methanol decrease some before it increase, while the selectivity to CO_2 increase before it decrease. This could be caused by other reaction occurring at the same time as the hydrolysis, forming by-product as CO. CO_2 are likely to be formed from CO and O_2, the selectivity to CO_2 is shown a decrease when the selectivity to CO increase. The mole% H_2 in the product stream is seen to reduce slow with time, H_2 can be part in a reaction at the whole test. Data for Figure 5-8 in Appendix 13.

45
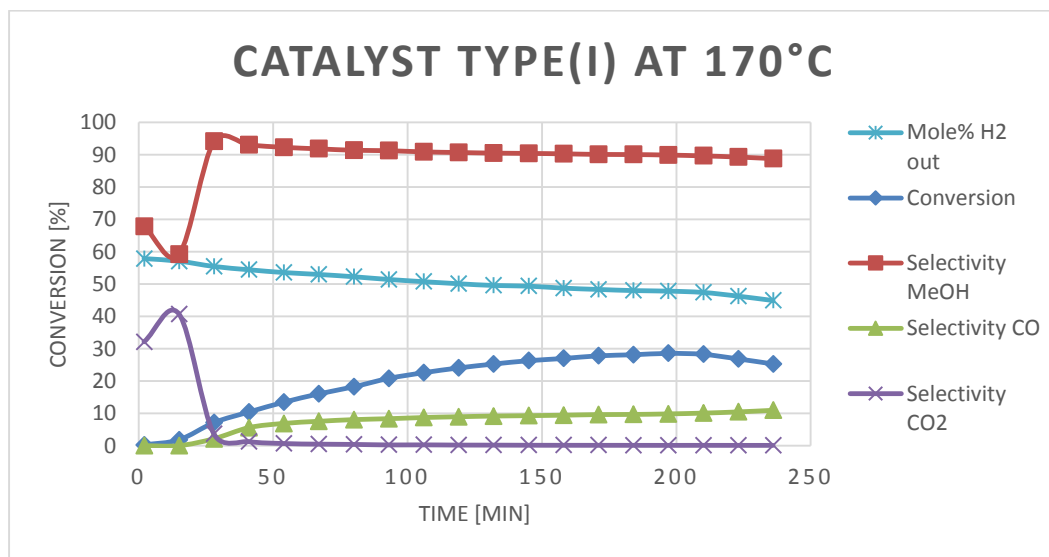
Figure 5-8: Conversion and selectivity to MeOH, CO and CO_2 and the mole% of H_2 in the product stream for catalyst Type (I), 1. Tested, at 170°C.

Figure 5-9 show the conversion and selectivity for methanol, CO and CO_2, and mole% H_2 in the product stream, for catalyst Type (I) at 210°C, with time. In the start of the test, O_2 is in the system. The selectivity to methanol increase after a short time, while the selectivity to CO_2 increase before it decreases. This show that the formation of methanol is low at the begging, probably caused by other reaction occur at the same time. The selectivity to methanol and CO increase when the conversion increase. The mole% H_2 concentration in the product stream starts high and starts decreasing when the selectivity to methanol increase and the selectivity to CO_2 decrease. This could imply that H_2 formed as a by-product the first 15 min in the test. The small decrease in one point for mole% H_2 out, measured around 200 min at the figure is a result of measurement errors. Data for Figure 5-9 in Appendix 14.
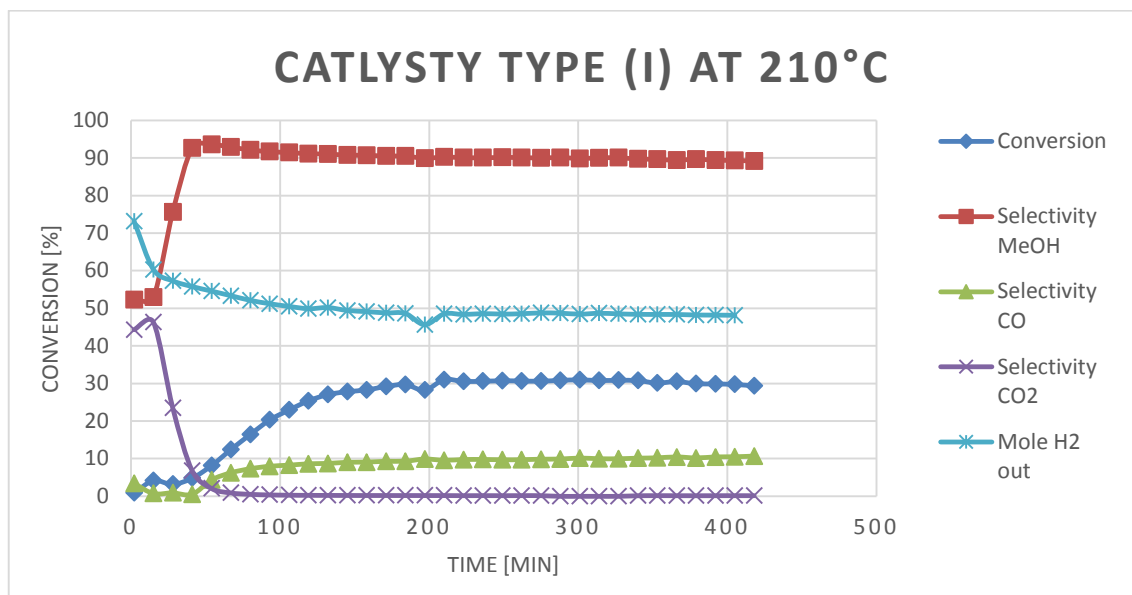
Figure 5-9: Conversion and selectivity to MeOH, CO and CO$_2$ and mole% of H$_2$ in the product stream for catalyst Type (I), 1. Tested, at 210°C.

Figure 5-10 show the conversion and selectivity to methanol, CO and CO$_2$, and mole% H$_2$ in the product stream, for catalyst Type (I) at 250°C, with time. In the start of the test, there is O$_2$ in the system. The selectivity to methanol increase after the start and then decrease some. This could be from other reaction occurring at the same time as the hydrolysis in the start. The conversion decreasing before increasing at the start is a result of mole% methyl formate in the product stream, increasing before it decrease. Mole% methanol in the product stream increase at the start and does not cause this drop-in conversion. The selectivity to CO follows the conversion and increase when the selectivity to CO$_2$ decrease. The mole% H$_2$ in the product stream starts high and starts decreasing when the selectivity to methanol increase and the selectivity to CO$_2$ decrease. It could be that H$_2$ is formed as a byproduct the first 54 min of the test. Data for Figure 5-10 in Appendix 15.
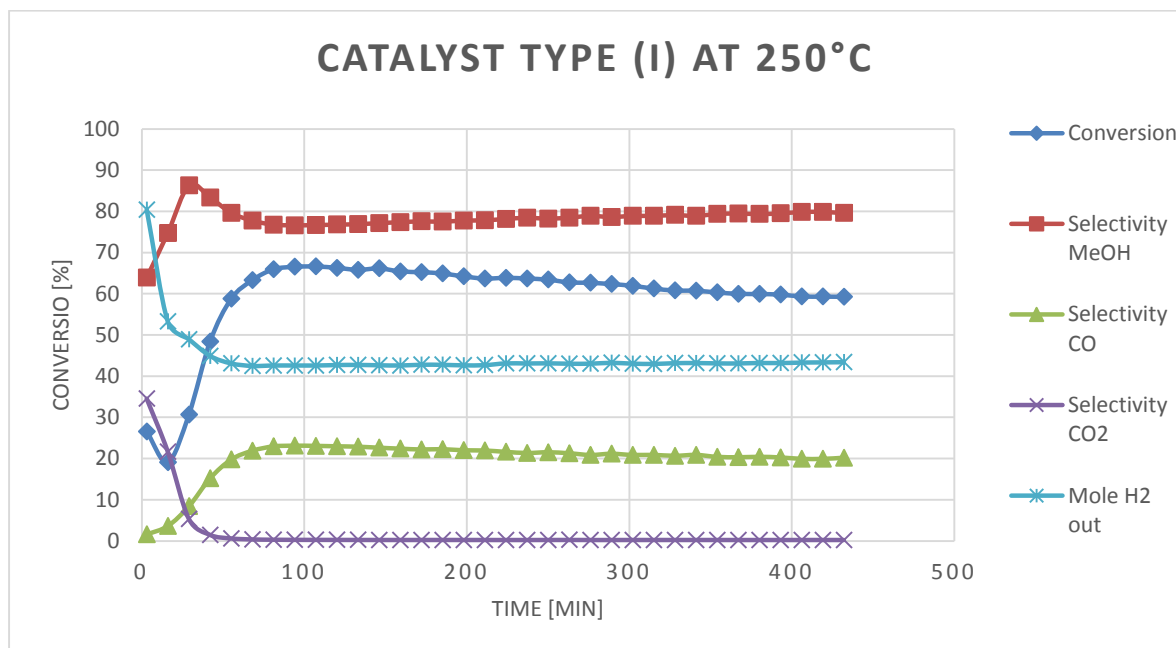
Figure 5-10: Conversion and selectivity to MeOH, CO and CO_2, and mole % H_2 in the product stream, for catalyst Type (I), 1. Tested, at 250°C.

Figure 5-11 show the conversion and selectivity to methanol, CO and CO_2, and mole% of H_2 in the product stream, for catalyst Type (II) at 250°C, with time. O_2 is in the system at the start of the test. The selectivity to methanol increase after the start and decrease some before it has a slow increase over time, while the selectivity to CO_2 quickly decrease to a low level. This could be from other reaction occurring at the same time as the hydrolysis in the start. The conversion show a decrease before it increase at the start, caused by increased mole% methyl formate in the product stream, and not a decrease in the mole% methanol. Mole% H_2 in the product stream is higher the first 41 min, this implies that H_2 could be produced as a by-product in the start of the test. The selectivity to CO follow the conversion and increase when the selectivity to CO_2 decrease. The increase in one point for conversion and mole% H_2 out after passed 300 min in time, is a result of measurement errors. Data for Figure 5-11 in Appendix 16.
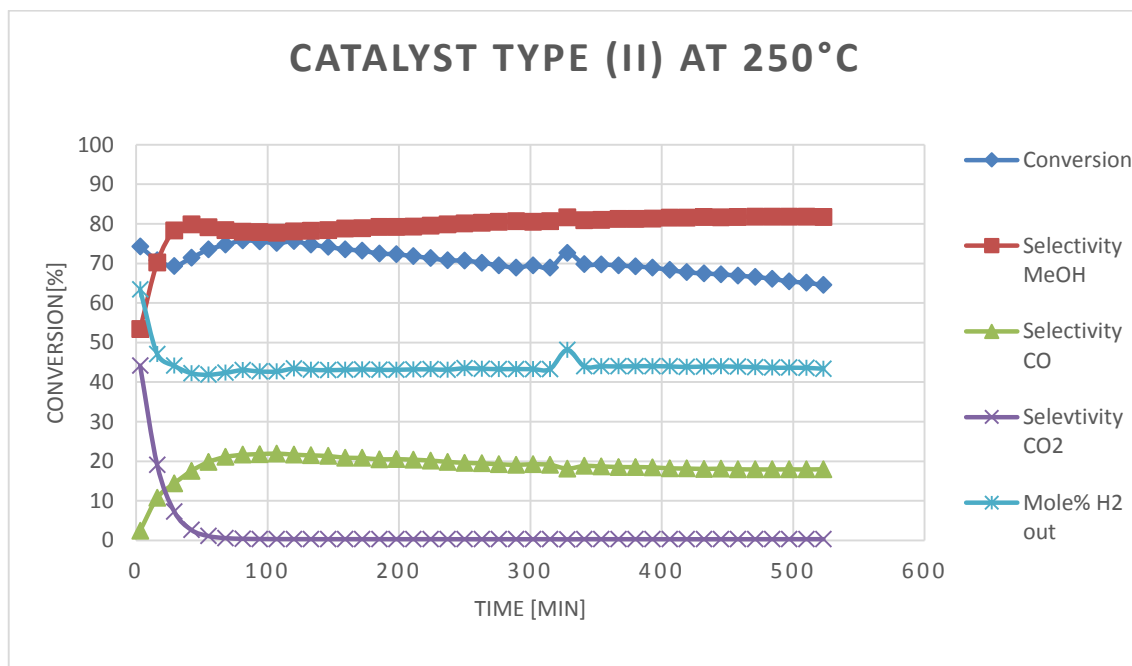
Figure 5-11: Conversion and selectivity to MeOH, CO and CO_2, and mole% H_2 in the product stream, for catalyst Type (II), 1. Tested, at 250°C.

5.7 Conversion and selectivity for catalyst Type (I) and Type (II)

Figure 5-12 shows the highest measured conversion for the catalyst Type (I) and Type (II) with the corresponding selectivity to methanol, CO and CO_2. Catalyst Type (I) at 170°C and 210°C has the highest selectivity to methanol, and the lowest selectivity to CO. Catalyst Type (I) has the highest measured conversion at 250°C and also the lowest selectivity to methanol at this temperature. For catalyst Type (I) and Type (II) at 250°C, the selectivity to methanol is the same, but lower compared to the catalyst at 170°C and 210°C. At 250°C, both catalyst also has higher selectivity to CO, compared to lower temperature. The selectivity to CO_2 is low at all temperature. Data for Figure 5-12 in Appendix 19.
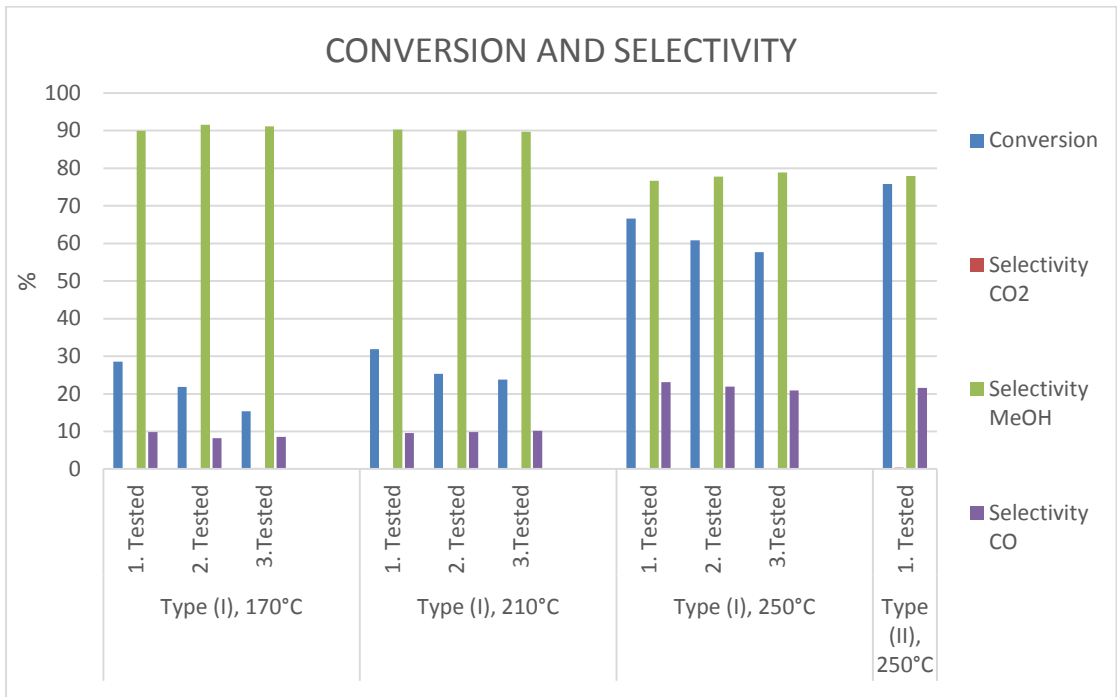
Figure 5-12: The highest measured conversion with the corresponding selectivity to MeOH, CO and CO2, for 1. Tested, 2. Tested and 3. Tested, with reactivation in between of each test.

6 Discussion

6.1 Error analyze:

The GC, is calibrated for methyl formate, methanol, H_2, N_2, CO and CO_2. In the analyze of the product stream there were no unknown peaks detected. O_2 is not detected in analyze of the product stream, it appears at the same time as N_2. There is a possibility that other components is not detected, due to column temperature and backflushing time.

For the calibration of the GC, the concentration of methyl formate and methanol was calculated based on partial pressure from the ideal gas law and vapor pressure. This simplification was made for practical reason, but this could give some deviation for the concentration.

The flow of methyl formate into the reactor is a calculated value and based on the assumption of ideal gas and that methyl formate is at a constant temperature of 0°C during the test. Conversion and selectivity are calculated from mole% in the product stream to avoid error from the calculated value of the flow of methyl formate into the reactor.

Methyl formate is placed in an ice bath, ice melting cause an increase in temperature and further an increase in the vapor pressure. Increased vapor pressure gives an increase in the flow of methyl formate into the reactor.

The response factor for the analyze on the GC is calculated from three points at the same flow and concentration. Thermal response values have earlier been determined for many hydrocarbons and some oxygenated compounds. Values who is independent of temperature, carrier gas, flow rate and concentration.[31] The relation between compounds has been compared to the same relations between the response factors of the compound in this calibration. There was some deviation when comparing relation between response factor to thermal response factor calculated by other.

There is no error measuring of the test data, the test was not repeated, due to practical reason. Calibration data at the same flow showed similar area for the peak and the curve show a similar progression, this indicates that the apparatus is working as it should.

The reaction temperature holds some error regarding the relation between the temperature of the oven and inside the wall of the reactor. Temperature measurement inside the reactor wall was done before the testing started. There could be some small deviation for the height of where the catalyst is placed since the reactor is packed manual with wool for each

test. How the catalyst distributes itself with distance to the wall is also unknown, and this could deviate between the tests.

6.2 Air in the system in the start of the test

At the start of a test the, there is air in the system. The reason for this is that methyl formate in liquid form is filled in a glass bottle who is connected to the system. The system has now possibility to be flushed with only N_2 when the glass bottle is filled with methyl formate. The glass bottle used in the testing has a total volume of 500 ml, at each experiment it was filled with 100ml of methyl formate. At the start of each test there is 400 ml of air in the glass bottle, this will mix with N_2 and methyl formate in the flow into the reactor. Air will leave the system with time. Figure 6-1 show the height of the peak of O_2 with time, detected in a flow of calibration gas and methyl formate through the system after start. There is no quantifying data for O_2, but the purpose is to see when O_2 is leaving the system. These data are obtained from earlier calibration method when O_2 was detected. After one hour, O_2 is seen to decrease to a third of the level from start.
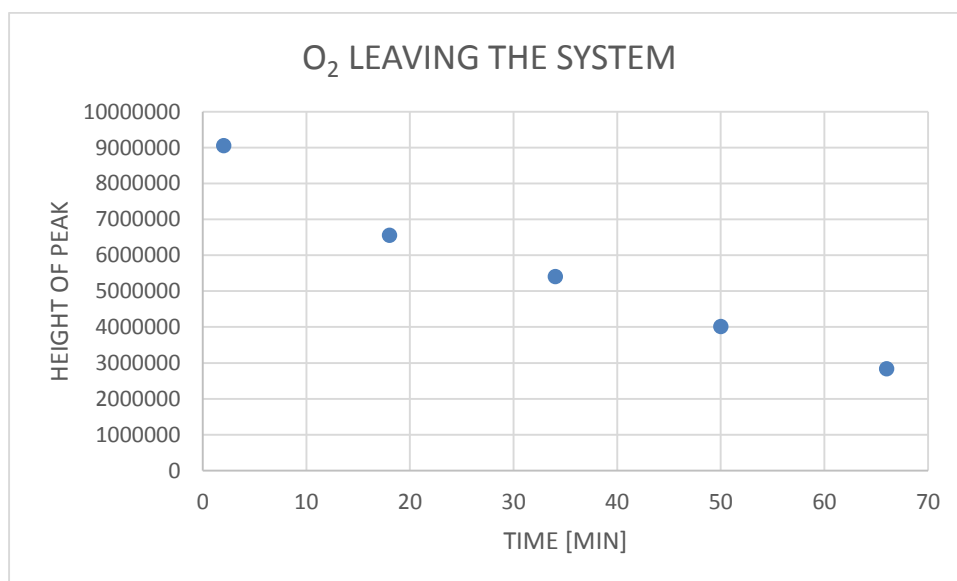

Figure 6-1: Oxygen in product stream versus time, detected in GC.

Oxygen in the start of a test may adsorb on the catalyst and react with CO. From the literature, copper is known to be a good oxidation catalyst. O_2 react with CO, reaction (R5-1).

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \hspace{4cm} \text{(R5-1)}$$

The first hour in the start of the test there is a high selectivity to CO_2, before it declines to a low level for the rest of the test. This coincides with the oxygen level seen in the figure. When the selectivity to CO_2 is high, the selectivity to CO is low, when the selectivity to CO_2 decreases the selectivity to CO increase.

6.3 Conversion

The highest conversion was found to be at 250°C for catalyst Type (II), this catalyst has larger surface area due to, smaller crystallite and particle size than Type (I). The composition of the two catalysts are different, but after the activation of the catalyst, the composition is uncertain.

Catalyst Type (I) has the highest conversion at 250°C, the conversion is at a lower level for temperature 170°C and 210°C. From the literature, a rule of thumb is that the reaction rate doubles with every 10°C the temperature increase. It can be assumed that the reaction goes faster at higher temperature.

The data for the test of catalyst Type (I) at 170°C is of short time. This was caused by an increase of methyl formate into the reactor, because ice in the ice bath for methyl formate melted, as explained earlier. The decrease in conversion at the end of the test for catalyst Type (I) at 170°C is a result of increased amount of methyl formate into the reactor. This gives higher mole% methyl formate in the product stream. The conversion is calculated from the mole% of the carbon atoms in the product stream, increased amount of methyl formate will reduce the calculated conversion. How fast it actually deactivate is not easy to determine, and because of practical reason, the test was not repeated.

Catalyst Type (I) at 210°C, in the first hour for the first test the conversion increase, decrease and increase again. This is caused by an increased amount of mole % methyl formate in the product stream. The mole% of methanol in the product stream is continuously increasing in the start. The conversion is seen to be stable with time.

Catalyst Type (I) at 250°C experience the same behavior with increase and decrease in conversion as catalyst Type (I) the first hour. At this temperature, this is also caused by an increase of mole% methyl formate in the product stream, while mole% methanol in product stream increase from the start. The conversion also show a slow decrease with

time, this behavior is not seen for conversion at a lower temperature and could be caused by sintering.

Catalyst type (II) at 250°C also show the same behavior as catalyst Type (I) at 250°C, with decrease and increase in conversion at the start of the test. However, the conversion starts at a higher level compared to catalyst Type (I) at the same temperature. This could be from different composition and smaller crystallite and particle size for catalyst Type (II) compared to catalyst Type (I).

Catalyst Type (I) was tested over a period of 2 days at 250°C. The test run was stopped on the evening of day 1, between the days the system was parked at a lower temperature, with close valves and pressure. Test data reported continuously. The conversion for both days followed the same decrease trend, and the conversion the second day started up in the same area as last measurement day 1. The decrease in conversion indicate that sintering occur for the catalyst at this temperature, the catalyst deactivate fast..

6.4 Catalyst Type (I) reactivated

Catalyst Type (I) was tested 3 times at 170°C, 210°C and 250°C, with activation of the catalyst in between of each test. A criterion for reactivating the catalyst was when the conversion of the catalyst went below 5%. The criteria were followed but after the testing, it was found that the loss in conversion was caused by an increased amount of methyl formate into the reactor. As mentioned earlier, methyl formate in a bottle was placed in an ice bath, melted ice caused increase temperature, resulting in an increase in the flow in to the reactor. This changed the ratio between H_2 and methyl formate, and mole% methyl formate increased in the product stream. The conversion calculated from concentration in the product stream reduces when the methyl formate increase.

Catalyst at all temperature experienced a decrease in the conversion between each test, the activation of the catalyst between the test did not give the catalyst the same activity as it had the test before.

The 3. test at 210° showed a slow decrease in conversion with time, this could indicate sintering of the catalyst.

Catalyst Type (I) at 250°C had a slow decrease in conversion with time, indicating that the catalyst have a decrease in conversion due to sintering at this temperature.

6.5 Selectivity

Reaction given below is believed to happen in the start of the tests.

Reaction (R5-1) the main reaction, hydrolysis of methyl formate to methanol.

$$HCOOCH_3 + 2H_2 \leftrightarrow 2CH_3OH \tag{R1-2}$$

Reaction (R2-1) and (R2-4) are reaction where only methyl formate reacts.

$$HCOOCH_3 \rightarrow CO + CH_3OH \tag{R2-1}$$

$$HCOOCH_3 \rightarrow 2CH_2O \tag{R2-4}$$

Hydrolysis of methyl formate to methanol and formaldehyde, in reaction (R2-6).

$$HCOOCH_3 + H_2 \rightarrow CH_2O + CH_3OH \tag{R2-6}$$

Formaldehyde reacts further in reaction (R2-7)

$$CH_2O \rightarrow CO + H_2 \tag{R2-7}$$

Reaction (R5-4) oxidation of CO.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{R5-1}$$
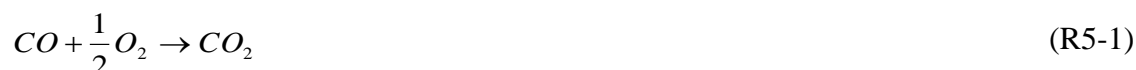
<u>Catalyst Type (I) at 170°C:</u>

At the beginning of the test, there is as mentioned earlier O_2 in the system. After 15 min in timeline the selectivity to methanol decrease while the selectivity to CO_2 increase, CO has no selectivity at this point. It is believed that CO is formed from methyl formate along with methanol. CO further oxidize to CO_2. This reaction competes with the hydrolysis. From the literature, it is found that CO does not replace methyl formate on the catalyst surface.CO can slow down the hydrolysis by taking available sites or replace H_2. Mole% H_2 in the product stream is decreasing slow with time, this indicates that it is part of a reaction and not formed at this temperature. It is difficult to measure if H_2 is formed in a reaction, since it is in the feed. After 28 min the selectivity to methanol is at its highest value and is on the same level the rest of the test. Selectivity to CO has started to increase while selectivity to CO_2 has decreased to almost zero, which seems reasonable if is formed by oxidation of CO. CO follows the conversion curve and it suggest that it is formed in the reaction for production of methanol.

Catalyst Type (I) at 210°C:

As mentioned earlier O_2 is in the system at the beginning of the test. After 28 min in timeline the selectivity to methanol increase, while the selectivity to CO_2 has increase after 15 min and starts decreasing after this point. CO has reduced from a low selectivity to zero after 15 min. The selectivity to CO starts increasing when the selectivity to CO_2 decrease. The selectivity to CO_2 is low the rest of the test.

It is believed that formaldehyde is formed from methyl formate and further reacts to CO and H_2 in this process. CO_2 is oxidize from CO and O_2 at the start.

In the start of the test mole% methyl formate in the product stream cause a small increase in conversion after 15min, then the conversion decrease before it stat increasing. This show that other reaction occur at the same time. An increase in unreacted methyl formate, along with increased selectivity to CO_2 indicates that the oxidation of CO is higher 15 min after start and this slows down the hydrolysis. As mentioned earlier the in the literature it's found that CO does not replace methyl formate on the surface of the catalyst. CO can replace H_2 on the surface of the catalyst or take available site, in this way CO slows down the hydrolysis of methyl formaten. Mole% H_2 in the product stream show a large decrease from 2 min to 15 min, and this indicate that H_2 is formed in the reaction. As mentioned earlier, it is difficult to measure if H_2 is formed in a reaction, since it is in the feed

Catalyst Type (I) at 250°C:

As mentioned O_2 is in the system at the beginning of the test. From the start of the test and until 28 min, selectivity to methanol increase, after this point it decrease some before it has a slow increase. In the first 28 min the selectivity to CO_2 decrease quickly in to nearly zero, and is low for the rest of the test. It assumed that CO_2 is oxidize from CO in the start. Selectivity to CO increase from the start at this temperature. It is believed that formaldehyde is formed from methyl formate and further reacts to CO and H_2 in the start of the test, since the mole% H_2 is high in the beginning of the test. As mentioned earlier formation of H_2 is difficult to measure. Comparing mole% H_2 in the product stream at 250°C, to mole% H_2 the product stream at 170°C, indicates that H_2 is formed in the start of the test at 250°C.

Increased mole% methyl formate in the product stream after 15 min cause a small increase in conversion at this point, it is reduced at the next point and the conversion starts increasing. This indicates that other reaction happens at the same time as the hydrolysis. It

could be that formaldehyde and methyl formate self-interacting in the start forming CO, H_2, methanol. CO follows the conversion curve and it indicates that it is formed in the reaction when methanol is formed.

Catalyst Type (II) at 250°C:

Show the same behavior as catalyst Type (I) at 250°C, a difference is that the selectivity to methanol do not reached the same high level after 28 min. The selectivity to methanol is at the same level at the rest of the test. Mole% H_2 in the product stream decrease some faster, than for catalyst Type (I), this indicates that H_2 is formed some time shorter than for catalyst Type (II). Conversion has same decrease in conversion in the start of the test, but starts higher. The selectivity CO increase faster in the beginning compared to catalyst Type (I) at 250°C. CO_2 has the same decrease in selectivity for both catalyst at 250°C. This indicates that more CO is formed in the start of the test for catalyst Type (II) at 250°C.

Selectivity to methanol is highest at 170°C and 210°C for catalyst Type (I), and has no change between the reactivation. The selectivity to CO is lowest at these temperatures. At 250°C both catalyst has the same selectivity to methanol and CO. Compared to the lower temperature the selectivity to CO is higher at this temperature. The literature recommend a reaction temperature below 500K (227°C) to avoid formation of CO. The increase in formation of CO is seen at 250°C, this decrease the selectivity to methanol.

Selectivity to CO_2 is low at all temperature for both catalyst during the test. In the beginning of a test the selectivity to CO_2 is high, at this time O_2 is present in the system. From the Figure 6-1 the oxygen level is seen to be reduce to a third the first hour.

At 170°C and 210°C for catalyst Type (I), the selectivity to CO_2 increase before it decrease in the start of the test. This probably caused by several reaction happening at the same time. CO_2 can be formed by oxidation of CO or from methyl formate.

7 Conclusion

The conversion increase with increased reaction temperature and the conversion of methyl formate is highest at 250°C.

Catalyst Type (II) has higher conversion at 250°C than catalyst Type (I).

Catalyst Type (I) deactivate faster at 250°C than 170°C and 210°C. At 250°C, both catalyst show the same decrease in conversion with time. The decrease in conversion at 250°C show sign of sintering but further investigation of the catalyst is needed to support this conclusion.

The reactivation of the catalyst between the tests do not give them the initial activity back.

The selectivity to methanol is higher at 170°C and 210°C compared to 250° for catalyst Type (I). Catalyst Type (I) and Type (II) has the same selectivity at 250°C. The selectivity is lower at 250°C because of increased formation of CO at this temperature

Air in the system in the beginning of each test effect the hydrolysis of methyl formate, and other reaction occur at the same time. O_2 react with the catalyst, and CO_2 is formed by CO oxidation.

H_2 is produced in the start at 250°C for both catalyst and at 210°C for catalyst Type (I)

8 Further work

The stability for catalyst Type (I) should be further tested. Catalyst Type (I) should be retested at 170°C, due to increased amount of methyl formate into the reactor interfered with the test in this work.

Catalyst Type (II) should be tested at the same temperature as catalyst Type (I) for comparing. The stability for catalyst Type (II) should also be tested at the same temperature as catalyst Type (I).

Catalyst Type (II) should by teste at reaction temperature of 160°C, to see if react at this temperature.

The catalyst should be tested in a system without O_2 in the process at the start of the test.

The catalyst should be tested at a different H_2/methyl formate ratio to see how it effect the conversion.

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Appendix

Appendix 1: Description of Master's Thesis

Telemark University College
Faculty of Technology

FMH606 Master's Thesis

<u>Title</u>: Hydrogenolysis of Methyl formate over copper nano particles

<u>TUC supervisor</u>: C. Ahoba-Sam/K.-J. Jens

<u>External partner</u>: none

<u>Task background</u>:

Methanol (MeOH) has been identified as a potential multipurpose molecule for energy and CO_2 storage [1]. It stores both carbon and hydrogen in the liquid form (MeOH b.p is 64.7 °C) which reduces transportation difficulties, is used as fuel by itself or blended with gasoline as well as for production of electricity by electrochemical oxidation of methanol [2]. MeOH can be directly converted into light olefins, gasoline and hydrocarbons over acidic zeolites [3], thereby providing alternatives for energy source and petrochemical feedstock.
MeOH is currently synthesized from syngas (made up of $CO/CO_2/H_2$) over solid acid catalysts. Industrially, Cu/ZnO catalysts technology is used which operates at 250 °C and 70-80 bars of pressure. Though this technology is highly optimized, it is still capital intensive, due to high energy cost, and thermodynamically limited. This is because conversion of syngas to methanol is exothermic as indicated by equation 1 and lower temperature condition is required to make full conversion per pass.

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.6 \text{ kJ/mol} \qquad 1$$

In view of this, low temperature approach to synthesize methanol was identified by Christiansen about a century ago [4] using Nickel alkoxide. This reaction proceed in two steps as illustrated with equation 2 and 3. The first step is catalyzed by alkali alkoxide while the second is catalyzed by the transition metal, which is also the rate limiting step. However this approach has failed to be industrialized mainly due to safety reasons [5], as $Ni(CO)_4$ is toxic.

$$CO + CH_3OH \leftrightarrow HCOOCH_3 \qquad 2$$
$$HCOOCH_3 + 2H_2 \leftrightarrow 2CH_3OH \qquad 3$$
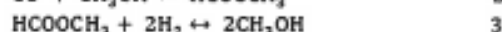
Copper alkoxide has also been identified to be active for low temperature methanol synthesis (LTMS) [6,7]. Our group has currently been working on copper alkoxide system in liquid phase for LTMS[8]. In this project, we will like to test the influence of different copper nano particles on hydrogenolysis of methyl formate at varying temperature in solid/liquid phase.

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## Task description:

Experimental program

January – Learn basic experimental skills such as: lab safety regulations, calibrate GC, learn how to press and sieve catalyst for testing.

February – Modify rig for experiment, initial testing with commercial sample to adjust reaction conditions.

March – Testing different catalyst Cu (nano) particles for methanol synthesis at varying temperature conditions.

April may, June: – Finalizing experiment and report

Simplified experimental set-up is as below
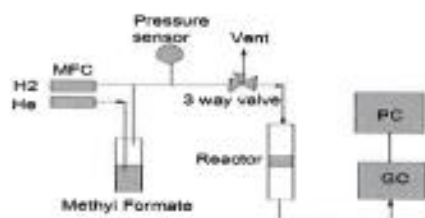
Student category: PT, EET students

Practical arrangements: Laboratory equipment is available

Signatures:

Student (date and signature): 01.02.2016 Hilde Hauge Amundsen

Supervisor (date and signature): Klaus-J. Jens
01.02.2016
01.02.2016

Appendix 2: Safe job analysis

SAFE JOB ANALYSIS

EXECUTED BY:
Hilde Hauge Amundsen

AREA:
B-194

DATE: 12.02.2016   **HSE - MSDS:**   YES ☐   NO ☐

PARTICIPANTS:	DEPARTMENT	SIGNATURE	PARTICIPANTS:	DEPARTMENT	SIGNATURE
Hilde H. Amundsen	PGM	Hildt Amundsen			
Christian Ahoskentin	PEM				
Wilson-John	PEO	Wilson-John			

NO	ACTIVITY DESCRIPTION	RISK DESCRIPTION	SAFETY MEASURES	RESPONSIBLE / DEADLINE
	Heating tape	Burn and electrical shock	Cover and insulate well	
	Catalysis, copper, nanoparticles.	Irritation of eyes, skin or nose. In contact with skin, it may enter the pores and react. Harmful or fatal if swallowed.	Use goggles and gloves. If contact with eye or skin, rinse immediately with water.	
	Hydrogen	Highly flammable, not visible flame. Explosive.	In case of fire, if possible close the valve on the H_2 bottle or remove it. Abandon the lab and alert.	
	Methanol and methyl formate	Highly flammable and almost invisible flame. Volatile. Toxic when inhaled, absorbed through skin or swallowed. Cause eye irritation.	In case of fire, extinguish if possible, or leave the room and alert. Were safety goggles and gloves.	
	CO_2 and N_2	Displacing air, may cause suffocation.	Good ventilation in the room.	

CO	Extremely flammable gas, making explosive mixture with air. Toxic if inhaled. May damage fertility and unborn child.	Leaking gas fire, do not extinguish, leave the room and alert. Leak test the system, before use. If inhaled, move to fresh air. Use gloves and goggles. In contact with eye or skin, rinse immediately with water. Good ventilation in the room.

Appendix 3: Temperature relation between oven and reactor

Temperature measured by thermometer [°C]	Set point oven[°C]	Temperature oven[°C]	Temperature measured by thermometer[°C]	Set point oven[°C]	Temperature oven[°C]	Length from the top of the oven [cm]
112	200	200				0
126	200	200				1
154	200	200	212	270	270	2
168	200	200	224	270	270	3
178	200	200	243	270	270	4
186	200	200	256	270	270	5
188	200	200	258	270	270	6
184	200	200	252	270	270	7
173	200	200	237	270	270	8
162	200	200	223	270	270	9
138	200	200				10
111	200	200				11

Thermometer standard ST-612 used for measuring the temperature inside the reactor wall, surrounded by the oven.

Appendix 4: Calibration data for MFC of N_2

Labwiev (ml/min)	Flowmeter (ml/min)
10	13
20	21
30	27
40	38
50	51
60	61
70	70
80	80
90	90
100	99
110	107
120	116

Appendix 5: Calibration of pressure measurement of the system

Pressure labwiev	Pressure manometer
0,048	0
0,1	0,1
0,2	0,2
0,3	0,35
0,4	0,5
0,5	0,6
0,6	0,75
0,7	0,9
0,8	1
0,9	1,2
1	1,4
1,1	1,5
1,2	1,6
1,3	1,85
1,4	2
1,5	2,1

Appendix 6: Vapor pressure, methyl formate and methanol

Methyl formate	
Temperature [K]	Vapor pressure [kPa]
262,35	15
267,69	20
276,12	30
282,34	40
287,39	50
291,69	60
295,43	70
298,77	80
301,79	90
303,2	95
304,29	99
304,55	100

Methanol	
Temperature [K]	Vapor pressure [kPa]
268,58	3
273,03	4
276,58	5
279,59	6
284,47	8
288,39	10
295,83	15
301,38	20
309,615	30
315,771	40
320,739	50
324,929	60
328,569	70
331,797	80
334,704	90
336,057	95
337,353	99
337,353	100

Appendix 7: Calculation and measured values, experimental work

Properties of the reactor:

h: 250 mm D: 9mm

$$V_{Rx} = \frac{\pi D^2}{4} \cdot h$$

$$V_{Rx} = 15904\,mm^3 = 15{,}904\,ml$$

Flow of methyl formate:

$$F_{MF} = \frac{P_{MF}}{P} \cdot F_{Total}$$

Partial pressure of methyl formate:

$$P_{MF} = P_{MF}^{\circ} - P_{MF}^{\circ} \cdot \frac{F_{H_2}}{F_{Total}}$$

Partial pressure of hydrogen:

$$P_{H_2} = \frac{F_{H_2}}{F_{Total}} \cdot P$$

Partial pressure of nitrogen:

$$P_{N_2} = \frac{F_{N_2}}{F_{Total}} \cdot P$$

Calculated pressure for the feed stream according to formula, listed in table below:

P°_{MF}	26,00kPa
P_{MF}	16,90kPa
P_{H2}	38,22kPa
P_{N2}	54,04kPa
F_{MF}	15,5ml/min

Measured values for the system in table below:

| T$_{MF}$	0°C
P	109,20kPa
F$_{N2}$	49,5ml/min
F$_{H2}$	35ml/min

H$_2$/ methyl formate ratio:

$$P_{H_2} \Big/ P_{methyl\ formate} = 38.2 \Big/ 16.9 = 2.3$$

Space velocity:

$$SV = \frac{100ml \cdot 10^{-6} m^3}{ml} \cdot \frac{g}{0,2g \cdot 10^{-3}} \cdot \frac{min}{60s} = 0,083 \frac{m^3}{kg \cdot s}$$

Appendix 8: Catalyst Type (I) and Type (II) XRD and TEM

Type 1
Cu_2O-15.9+_0.5

Type 2
CuO- 4.5+_0.1 nm

type 2

type 1

Intensity

2 theta (^{o})

Catalyst Type (I)

Catalyst Type (II)

50 nm

100 nm
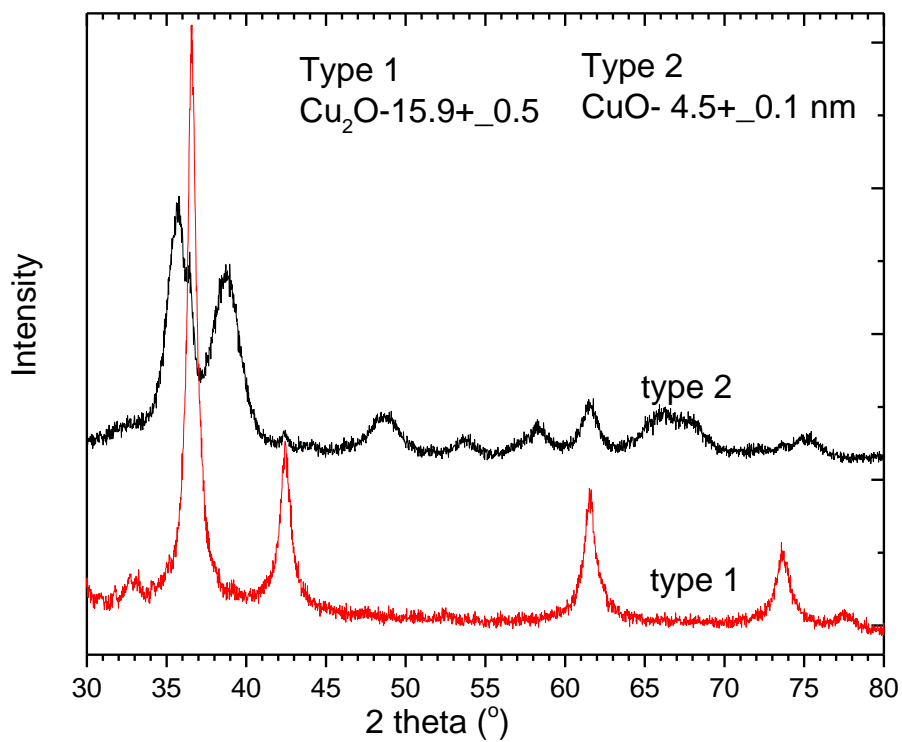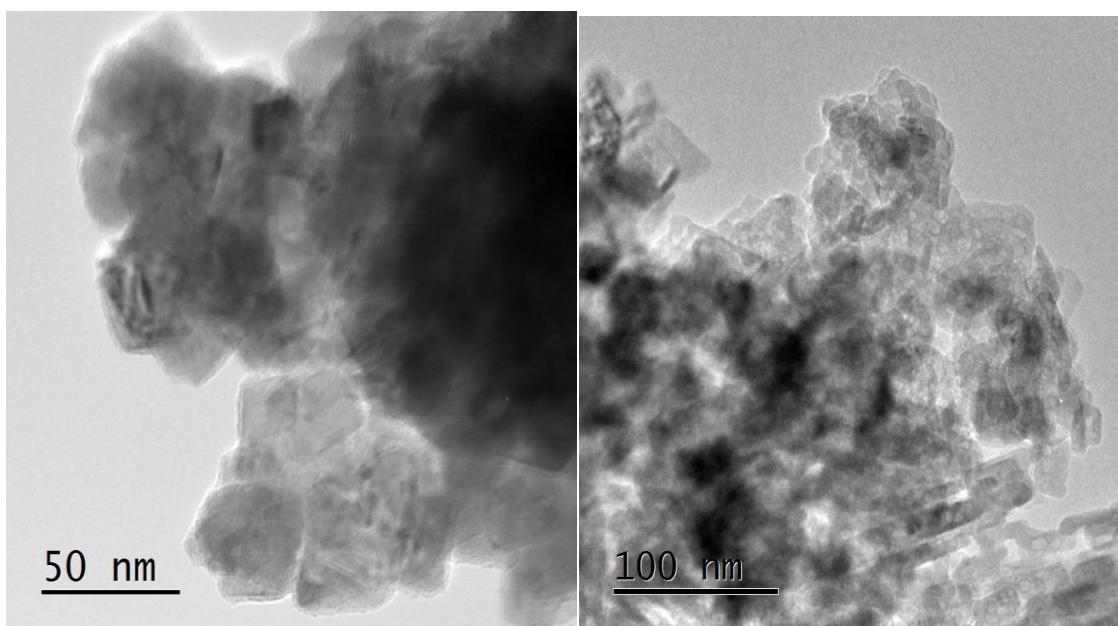
Appendix 9: Method for the GC analyze

Inlet:

Pressure: 2 psi

Temperature: 300°C

Purge flow: 1ml/min

Split ratio: 7,8514:1

Injection size: 0,2μl

Column:

Pressure: 40 psi

Event:

Injection time: From 0,01-3min

Backflush time from 1,6-9 min

The oven:

Temperature programming:

Initial: temperature 130°C, hold time 2 min

Ramp 1: rate of 25°C/min, temperature 200°C, hold time of 1 min.

Ramp 2: rate of 25°C/min, temperature 130°C, hold time of 3,4 min

TCD:

Heater: 150°C

Reference flow: 45 ml/min

Make up flow: 2ml/min

Inlet pressure: 70 psi

Appendix 10: Calibration data

Component	H_2	CO_2	MeOH	MF	N_2	CO
Calibration area 1	6,03E+06	2,42E+08	8,77E+08	2,02E+09	2,42E+09	3,62E+08
Calibration area 2	5,98E+06	2,46E+08	8,71E+08	2,01E+09	2,41E+09	3,66E+08
Calibration area 3	5,96E+06	2,44E+08	8,77E+08	2,02E+09	2,4E+09	3,7E+08
Average area	5,99E+06	2,44E+08	8,75E+08	2,02E+09	2,41E+09	3,66E+08
Standard deviation	0,559909	0,785170	0,397772	0,294338	0,556550	1,101546
Concentraition [Mole %]	15,24	3,81	11,95	23,81	49,52	7,62
Respons factor	2,54E-06	1,56E-08	1,36E-08	1,18E-08	2,05E-08	2,08E-08

$$RF = \frac{Concentraition}{Area}$$

Comparing relation between components response factor from the calibration to thermal response found by Rosie and Grob.

Components relation	Responce factor	Thermal responce factor
MeOH/CO	0,87356	1,14583
N_2/CO_2	0,98706	1
CO/CO_2	0,75082	1,14286

Appendix 11: Conversion for catalyst Type (I)

1. Tested at 170°C, 210°C and 250°C

Time	Temperature		
min	170°C	210°C	250°C
2	1,803196	0,902201	26,54283
15	7,141323	4,130076	19,1131
28	10,41642	3,18952	30,69429
41	13,466	4,808532	48,36279
54	16,04819	8,165683	58,77576
67	18,24809	12,43159	63,28804
80	20,84283	16,46098	65,92159
93	22,6104	20,30302	66,54063
106	24,09452	22,96912	66,61366
119	25,30062	25,39965	66,27831
132	26,33508	27,06731	65,80338
145	27,02474	27,84709	66,13691
158	27,85034	28,30307	65,426
171	28,18231	29,21935	65,21843
184	28,60398	29,73063	64,91818
197	28,3147	28,25553	64,19783
210	26,90777	31,01817	63,68082
223	25,32781	30,59995	63,85597
236		30,6133	63,68862
249		30,75817	63,41214
262		30,68604	62,75231
275		30,64046	62,64658
288		30,85953	62,33719
301		30,98741	61,92166
314		30,81596	61,24353
327		30,86452	60,7818
340		30,79945	60,722
353		30,13719	60,30807
366		30,54467	59,9761
379		29,95726	59,9206
392		29,91733	59,78376
405		29,76015	59,33367
418		29,41182	59,29463

Appendix 12: Conversion for catalyst Type (I) and Type (II) at 250°C

Time [min]	Type (I)	Type (II)
2	26,54283	74,29305
15	19,1131	70,79037
28	30,69429	69,34172
41	48,36279	71,41429
54	58,77576	73,50325
67	63,28804	74,71128
80	65,92159	75,79304
93	66,54063	75,56404
106	66,61366	75,10973
119	66,27831	75,59891
132	65,80338	74,74176
145	66,13691	74,17555
158	65,426	73,5612
171	65,21843	73,19634
184	64,91818	72,49889
197	64,19783	72,298
210	63,68082	71,82977
223	63,85597	71,32576
236	63,68862	70,7608
249	63,41214	70,7204
262	62,75231	70,16135
275	62,64658	69,52202
288	62,33719	68,91304
301	61,92166	69,52126
314	61,24353	68,91615
327	60,7818	72,68133
340	60,722	69,79357
353	60,30807	69,7544
366	59,9761	69,48493
379	59,9206	69,21915
392	59,78376	68,93808
405	59,33367	68,32917
418	59,29463	67,76344
431	59,25824	67,46006
444	58,79685	67,23658
457		66,91481
470		66,56137
483		66,11463
496		65,43904
509		65,11513
522		64,52454

Appendix 13: Catalyst Type (I) at 170°C

Time [min]	Conversion at 170°C			Catalyst 1.Teste at 170°C			
	1. Tested	2. Tested	3. Tested	Selectivity CO_2	Selectivity MeOH	Selectivity CO	Mole% H_2 in product stream
2	0,236322	0,605892	0,517527	34,85242	67,85248	0	57,90431
15	1,803196	0,88886	0,645999	32,14752	59,2576	0	57,10446
28	7,141323	2,015337	0,684058	40,7424	94,16463	2,147923	55,47225
41	10,41642	1,693597	1,841107	3,687451	93,06536	5,598241	54,45771
54	13,466	2,743447	2,094694	1,336402	92,35125	6,907346	53,59437
67	16,04819	16,11862	5,928386	0,741399	91,88236	7,567454	53,00972
80	18,24809	18,71224	9,03611	0,550189	91,44924	8,084652	52,29524
93	20,84283	20,13322	11,9758	0,466108	91,31333	8,378885	51,45734
106	22,6104	20,91125	13,39356	0,307785	90,94104	8,732663	50,77957
119	24,09452	21,31317	14,29664	0,326299	90,75058	8,983069	50,14288
132	25,30062	21,54295	14,87903	0,266347	90,56413	9,192654	49,60619
145	26,33508	21,78967	15,15924	0,243211	90,47544	9,313185	49,39771
158	27,02474	21,86859	15,30215	0,211377	90,34617	9,460499	48,77975
171	27,85034	21,9054	15,26759	0,193335	90,16004	9,647784	48,37883
184	28,18231	21,83742	15,34841	0,192179	90,12066	9,697237	48,02512
197	28,60398	21,6677	15,24282	0,182106	89,96384	9,861221	47,86545
210	28,3147	21,56202	15,01489	0,17494	89,71287	10,10557	47,44988
223	26,90777	21,31839	14,51777	0,181557	89,349	10,48222	46,31068
236	25,32781	21,00449	13,96751	0,168783	88,8536	10,97727	44,96412
249		20,63139	13,16912	0,16913			
262			12,14598				

Appendix 14: Catalyst Type (I) at 210°C

Time [min]	Conversion at 210°C			Catalyst 1.Teste at 210°C			
	1. Tested	2. Tested	3. Tested	Selectivity CO_2	Selectivity MeOH	Selectivity CO	Mole% H_2 in product stream
2	0,902201	0,725212	1,294088	44,31222	52,29415	3,393624	73,15475
15	4,130076	1,008415	1,643939	46,2892	52,98407	0,726735	60,29893
28	3,18952	1,125738	2,818625	23,46729	75,6453	0,887416	57,2742
41	4,808532	3,349358	2,30763	6,800486	92,67336	0,526159	55,76489
54	8,165683	2,903812	2,861854	2,07101	93,61032	4,318667	54,5568
67	12,43159	5,682806	9,319314	0,891798	92,89439	6,21381	53,32834
80	16,46098	9,316721	14,78777	0,526235	92,17711	7,296653	52,09967
93	20,30302	12,57894	17,67197	0,369888	91,68594	7,944176	51,1974
106	22,96912	15,11346	19,71712	0,294655	91,47067	8,234676	50,47951
119	25,39965	17,17987	20,92743	0,259763	91,14563	8,594611	49,87576
132	27,06731	18,58333	21,92103	0,240726	91,06218	8,697096	50,16725
145	27,84709	19,60655	22,54678	0,226113	90,78142	8,992463	49,4155
158	28,30307	21,09729	23,21255	0,21225	90,73682	9,050926	49,10233
171	29,21935	22,03723	23,14859	0,209504	90,53127	9,259221	48,75759
184	29,73063	22,97638	23,60441	0,205376	90,50722	9,287402	48,61231
197	28,25553	23,17118	23,64031	0,200909	89,94784	9,851254	45,60614
210	31,01817	23,57803	23,54765	0,196368	90,26074	9,542894	48,50266
223	30,59995	24,04464	24,00067	0,172027	90,10458	9,723391	48,33835
236	30,6133	24,31424	23,82975	0,180964	90,07244	9,746599	48,57106
249	30,75817	24,48223	23,80087	0,171103	90,16222	9,666679	48,44141
262	30,68604	24,81459	23,68731	0,181194	90,13034	9,688465	48,54527
275	30,64046	25,04163	23,61673	0,172294	90,0099	9,817807	48,75588
288	30,85953	25,19586	23,65274	0	90,14368	9,856319	48,69276
301	30,98741	25,38598	23,45404	0	89,88667	10,11333	48,42912
314	30,81596	25,25853	23,14696	0	90,06199	9,938012	48,66402
327	30,86452	25,04049	22,89359	0	90,06884	9,931159	48,50213
340	30,79945	25,22302	22,85845	0,150858	89,75906	10,09008	48,38162
353	30,13719	25,34686	22,65592	0,174539	89,65122	10,17424	48,35401
366	30,54467	24,84993	22,4663	0,164554	89,42264	10,4128	48,34483
379	29,95726	25,07768	22,22868	0,156374	89,68867	10,15496	48,20197
392	29,91733	24,88152	21,87786	0,16571	89,42016	10,41413	48,17374
405	29,76015	24,38283	21,65147	0,169513	89,37135	10,45914	48,12093
418	29,41182	24,54934	21,52064	0,165167	89,19817	10,63667	48,04258
431			21,30934				
444			20,8248				
457			20,69662				
470			20,42982				
483			19,88792				
496			19,24787				

Appendix 15: Catalyst Type (I) at 250°C

| Time [min]	Conversion at 250°C			Catalyst 1.Teste at 250°C			
	1. Tested	2. Tested	3. Tested	Selectivity CO2	Selectivity MeOH	Selectivity CO	Mole% H_2 in product stream
2	26,54283	44,68032	20,04642	34,5155	63,91542	1,569081	80,39366
15	19,1131	34,27969	20,06342	21,63842	74,739	3,62258	53,2352
28	30,69429	31,69809	29,29595	5,30177	86,28966	8,408569	48,9445
41	48,36279	40,08417	41,16075	1,467926	83,34803	15,18405	44,90795
54	58,77576	49,58401	49,35553	0,611025	79,62528	19,76369	43,08459
67	63,28804	55,77469	53,9784	0,372238	77,73774	21,89002	42,47759
80	65,92159	59,73812	55,98942	0,300815	76,75093	22,94825	42,5813
93	66,54063	60,84104	56,86355	0,269518	76,61001	23,12048	42,58249
106	66,61366	60,77069	56,63658	0,260675	76,66202	23,0773	42,58083
119	66,27831	59,80154	57,67573	0,253862	76,77295	22,97318	42,6948
132	65,80338	59,3439	57,59902	0,24231	76,88168	22,87601	42,72349
145	66,13691	58,65822	57,4168	0,237603	77,13476	22,62764	42,63611
158	65,426	58,23256	56,92768	0,23518	77,36147	22,40335	42,58401
171	65,21843	57,60234	56,86433	0,234158	77,56156	22,20428	42,76285
184	64,91818	56,73422	56,4541	0,240723	77,4829	22,27637	42,74754
197	64,19783	56,22436	55,81336	0,237694	77,7601	22,0022	42,61527
210	63,68082	55,62149	55,69088	0,232136	77,8113	21,95656	42,66373
223	63,85597	54,97592	55,4358	0,230389	78,15024	21,61937	43,09895
236	63,68862	52,12435	54,86864	0,22749	78,4192	21,35331	43,07047
249	63,41214	56,35443	54,62566	0,237933	78,23295	21,52912	43,11124
262	62,75231	56,92403	54,35586	0,242902	78,47499	21,28211	43,01246
275	62,64658	56,62247	53,56937	0,229039	78,8957	20,87526	43,01947
288	62,33719	56,38277	54,93134	0,225641	78,61668	21,15768	43,2315
301	61,92166	56,17129	49,78344	0,23336	78,89391	20,87273	43,03355
314	61,24353	56,32942		0,233453	78,8774	20,88914	42,96273
327	60,7818	56,4039		0,232831	79,1012	20,66597	43,14648
340	60,722	56,28045		0,232366	78,88256	20,88507	43,18131
353	60,30807	55,84822		0,234252	79,35511	20,41064	43,09406
366	59,9761	55,19285		0,2269	79,45456	20,31854	43,077
379	59,9206	54,07079		0,231126	79,34593	20,42295	43,19293
392	59,78376	53,28576		0,226911	79,50017	20,27292	43,17252
405	59,33367	52,7232		0,230876	79,84004	19,92909	43,28881
418	59,29463	52,72557		0,233669	79,84522	19,92111	43,33597
431	59,25824	52,02202		0,229915	79,57055	20,19954	43,38374
444		51,29166					
457		49,74644					

Appendix 16: Catalyst Type (II) at 250°C

Catalyst 1.Teste at 250°C					
Time [min]	Conversion	Selectivity CO$_2$	Selectivity MeOH	Selectivity CO	Mole% H$_2$ in product stream
2	74,29305	44,1398	53,41329	2,446915	63,44261
15	70,79037	19,04336	70,20989	10,74675	47,11034
28	69,34172	7,268647	78,33742	14,39394	44,11968
41	71,41429	2,634477	79,82202	17,5435	42,24133
54	73,50325	1,082766	79,11019	19,80704	41,86283
67	74,71128	0,56675	78,34632	21,08693	42,33991
80	75,79304	0,400153	77,97533	21,62452	43,01649
93	75,56404	0,340077	77,87731	21,78261	42,68501
106	75,10973	0,31874	77,74229	21,93897	42,67605
119	75,59891	0,312041	78,03176	21,6562	43,39366
132	74,74176	0,305861	78,21606	21,47808	43,09826
145	74,17555	0,295792	78,38363	21,32058	43,02231
158	73,5612	0,300856	78,80847	20,89067	43,10778
171	73,19634	0,299677	78,88045	20,81987	43,22313
184	72,49889	0,300069	79,22198	20,47795	43,08932
197	72,298	0,293806	79,1831	20,5231	43,11168
210	71,82977	0,299485	79,31603	20,38448	43,21438
223	71,32576	0,3028	79,53396	20,16324	43,22976
236	70,7608	0,294468	79,86637	19,83916	43,13668
249	70,7204	0,29043	80,12452	19,58505	43,49516
262	70,16135	0,29112	80,24856	19,46032	43,39001
275	69,52202	0,297589	80,45919	19,24322	43,26749
288	68,91304	0,28253	80,62946	19,08801	43,30199
301	69,52126	0,293982	80,4621	19,24392	43,26772
314	68,91615	0,296987	80,61777	19,08524	43,30108
327	72,68133	0,26008	81,60693	18,13299	48,15628
340	69,79357	0,293786	80,90621	18,8	43,97859
353	69,7544	0,299481	81,00185	18,69867	44,00846
366	69,48493	0,289853	81,17851	18,53163	43,95864
379	69,21915	0,298898	81,18585	18,51525	44,0121
392	68,93808	0,289818	81,26522	18,44496	44,02753
405	68,32917	0,28813	81,50289	18,20898	43,96662
418	67,76344	0,289093	81,55872	18,15219	43,82767
431	67,46006	0,274713	81,66476	18,06053	43,93627
444	67,23658	0,299181	81,59143	18,10939	43,97147
457	66,91481	0,289001	81,74384	17,96716	43,88605
470	66,56137	0,28618	81,78515	17,92867	43,76939
483	66,11463	0,296884	81,78073	17,92238	43,63851
496	65,43904	0,298791	81,75422	17,94699	43,6356
509	65,11513	0,29604	81,7838	17,92016	43,59609
522	64,52454	0,303442	81,72585	17,97071	43,37351

Catalyst teste at 250°C over several days							
Time[min]	Conversion	Time[min]	Conversion	Time[min]	Conversion	Time[min]	Conversion
2	26,54283	537	51,15607	1072	53,38966	1605	41,73359
15	19,1131	550	49,81115	1085	53,98022	1618	39,90762
28	30,69429	563	52,27737	1098	53,74631		
41	48,36279	576	52,21302	1111	53,57382		
54	58,77576	589	51,84647	1124	54,08717		
67	63,28804	602	51,70099	1137	59,80229		
80	65,92159	615	51,14079	1150	61,29811		
93	66,54063	628	50,95332	1163	60,5342		
106	66,61366	641	51,22777	1176	60,3105		
119	66,27831	654	51,57096	1189	59,69541		
132	65,80338	667	51,59495	1202	58,62959		
145	66,13691	680	51,41835	1215	57,32568		
158	65,426	693	51,19702	1228	55,10582		
171	65,21843	706	51,25671	1241	50,23645		
184	64,91818	719	50,80671	1254	50,77235		
197	64,19783	732	50,82322	1267	50,78452		
210	63,68082	745	50,83395	1280	50,20409		
223	63,85597	758	50,28204	1293	50,06607		
236	63,68862	771	49,75685	1306	49,74054		
249	63,41214	784	50,39332	1319	50,88126		
262	62,75231	797	50,04953	1332	50,59314		
275	62,64658	810	49,636	1345	48,43653		
288	62,33719	823	49,33655	1358	48,36203		
301	61,92166	836	48,96255	1371	47,83402		
314	61,24353	849	48,60678	1384	47,55949		
327	60,7818	862	48,49392	1397	47,36537		
340	60,722	875	48,16794	1410	46,89895		
353	60,30807	888	47,26445	1423	46,60212		
366	59,9761	901	46,49275	1436	46,07713		
379	59,9206	914	46,12699	1449	45,401		
392	59,78376	927	46,81553	1462	44,88678		
405	59,33367	940	45,43597	1475	44,93174		
418	59,29463	953	44,58345	1488	43,80841		
431	59,25824	968	27,8111	1501	45,78348		
444	58,79685	981	33,90823	1514	45,75235		
459	26,87628	994	41,30012	1527	40,40104		
472	36,71729	1007	46,26208	1540	45,17208		
485	46,45025	1020	49,25868	1553	43,84643		
498	48,81503	1033	50,99434	1566	43,41733		
511	50,3774	1046	52,55089	1579	43,08068		
524	51,47992	1059	53,54612	1592	42,17535		

CATALYST TYPE (I) AT 250°C
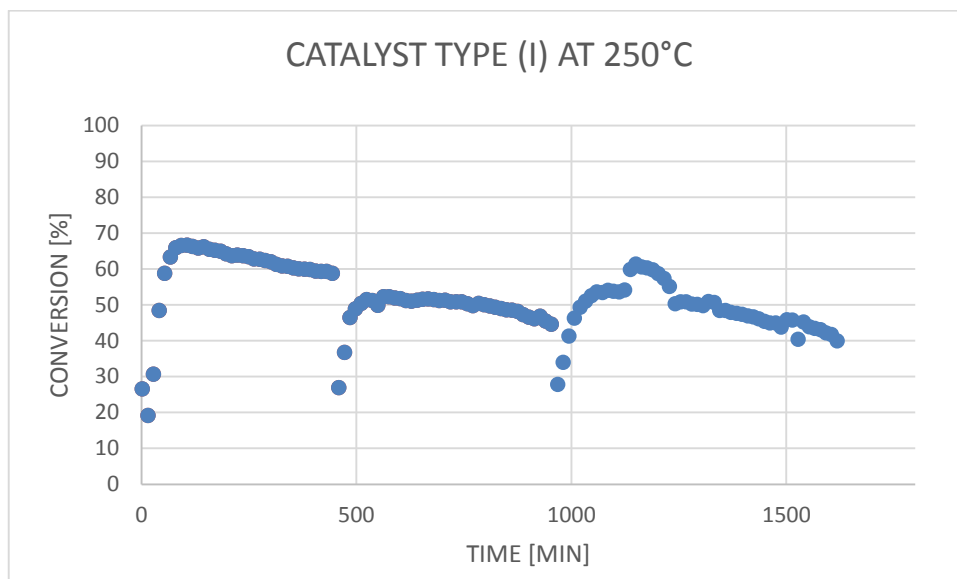
Appendix 18: Catalyst Type (II) at 250°C

Catalyst 1.Teste at 250°C			
Time [min]	Conversion	Time [min]	Conversion
2	74,29305	535	56,55414
15	70,79037	548	54,96213
28	69,34172	561	60,28584
41	71,41429	574	69,42881
54	73,50325	587	78,22535
67	74,71128	600	83,67945
80	75,79304	613	86,535
93	75,56404	626	87,60419
106	75,10973	639	87,71597
119	75,59891	652	87,53794
132	74,74176	665	87,25017
145	74,17555	678	89,81451
158	73,5612	691	89,01766
171	73,19634	704	88,80839
184	72,49889	717	88,90124
197	72,298	730	88,68944
210	71,82977	743	88,56134
223	71,32576	756	88,24241
236	70,7608	769	88,28434
249	70,7204	782	88,09287
262	70,16135	795	88,11985
275	69,52202	808	88,06185
288	68,91304	821	87,91871
301	69,52126	834	87,92785
314	68,91615	847	87,82066
327	72,68133	860	88,45079
340	69,79357	873	88,24648
353	69,7544	886	88,20746
366	69,48493	899	88,16812
379	69,21915	912	88,02574
392	68,93808	925	87,95233
405	68,32917	938	87,97076
418	67,76344	951	87,89248
431	67,46006	964	87,79234
444	67,23658	977	87,57367
457	66,91481	990	87,53023
470	66,56137	1003	87,29026
483	66,11463	1016	87,07866
496	65,43904	1029	86,58149
509	65,11513	1042	86,40066
522	64,52454		

CATALYST TYPE (II) AT 250 °C
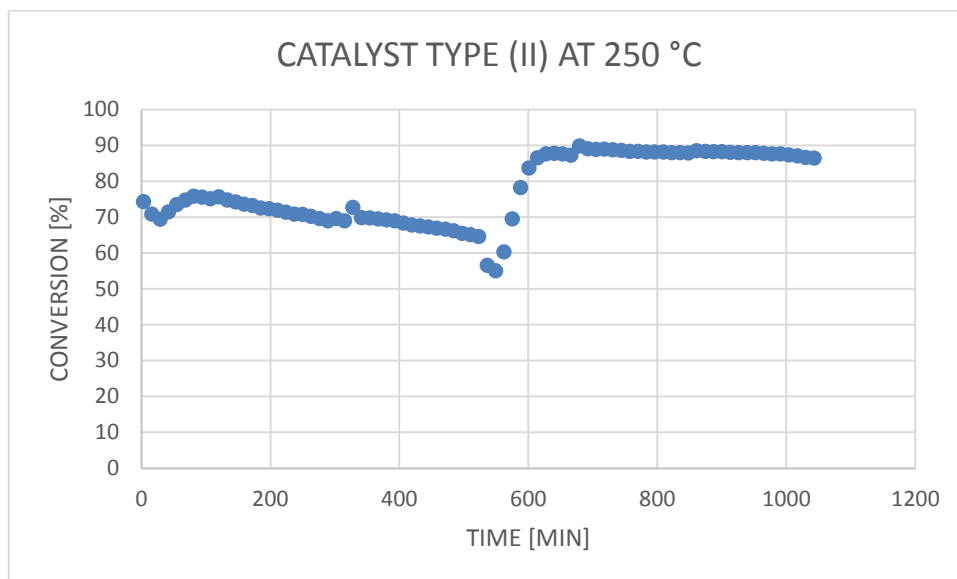
Appendix 19: Highest measured conversion and corresponding selectivity

Catalyst type and reaction temperature	Conversion	Time [min]
Type(I), 170°C 1.Tested	28,6	26
Type(I), 170°C 2.Tested	21,9	65
Type(I), 170°C 3.Tested	15,3	52
Type(I), 210°C, 1.Tested	31	169
Type(I), 210°C, 2.Tested	21,9	156
Type(I), 210°C 3.Tested	15,3	103
Type(I), 250°C, 1.Tested	66,6	39
Type(I), 250°C 2.Tested	60,8	39
Type(I), 250°C 3.Tested	57,7	39
Type(II), 250°C, 1.Tested	75,8	52

Catalyst type and reaction temperature		Conversion	Selectivity CO_2	Selectivity MeOH	Selectivity CO
Type (I), 170°C	1. Tested	28,6	0,18	89,96	9,86
	2. Tested	21,87	0,18	91,59	8,23
	3.Tested	15,35	0,314	91,12	8,56
Type (I), 210°C	1. Tested	31,92	0,2	90,26	9,54
	2. Tested	25,35	0,15	90,02	9,83
	3.Tested	23,83	0,14	89,71	10,15
Type (I), 250°C	1. Tested	66,61	0,26	76,66	23,08
	2. Tested	60,84	0,28	77,79	21,92
	3.Tested	57,67	0,21	78,86	20,93
Type (II), 250°C	1. Tested	75,8	0,4	77,98	21,62