

Setup and control of a test reactor for catalysis with optical access

Bachelor thesis

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Author
Christoffer Pichler

Supervisor
Johan Zetterberg



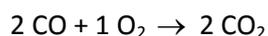
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Table of content

1. Introduction.....	2
2. Experimental methodology	5
2.1 Laser Induced Fluorescence	5
2.1.1 Background subtraction	6
2.2 Gas analysis	8
2.3 Temperature analysis	9
3. Experimental setup.....	12
3.1 Reactor	12
3.1.1 Heating cross	13
3.1.2 Gas supply system	13
3.2 Lasers.....	14
3.3 Mass spectrometer.....	14
3.4 IR cameras	15
4. Regulation technique	16
4.1 Loop controlled program.....	16
4.2 PID.....	16
5. Preparatory measurements	20
5.1 Excitation scan.....	20
5.2 Delay time.....	23
5.3 Integration time.....	24
5.4 LIF signal dependence on CO ₂ partial pressure	25
5.5 Temperature compensation.....	26
6. Catalytic measurements.....	28
6.1 One catalyst measurements.....	28
6.2 Two catalysts measurements	30
7. Conclusion	32
8. Outlook.....	33
Appendix A – self reflection	34
En lysande studie om katalysatorer.....	36
Appendix C – In depth programming	37
References.....	39

1. Introduction

The uses of catalysts are spread to many everyday life applications. Catalysts are used to speed up reactions by reducing energy barriers in the reaction path. Studying the CO oxidation to CO₂ on catalysts has applications not only limited to academic studies but also concerning car exhausts and other industrial processes. Therefore understanding how catalysts work is an important task. In this thesis the CO oxidation on pressed powder catalysts with 2% Pd, with CeO_x as support and 1% Pd, 2% Pt in CeO_x, were studied as a function of temperature. The CO oxidation can be described by the global reaction



and we have chosen to follow the product CO₂ with laser induced fluorescence at different reaction conditions combined with traditional analytics.

Traditionally the field of catalysis studies is divided into two major areas where reactivity or the surface of the catalyst is examined. The reactivity can be studied by examining the gas phase after the catalyst with a mass spectrometer (MS) [1], using Fourier transformed infrared spectroscopy (FTIR) [2] or gas chromatography (GC) [2]. The MS can measure several gases at the time (or more precisely, closely after each other) making it a convenient tool to measure both products and reactants at the same time with good temporal resolution, around 0.1s between each measurement point (if the MS measures three masses it would be 0.3s between measurements of the same mass). FTIR uses a polychromatic light source, e.g. a black body radiator, and with the use of beam splitters and mirrors, combines the light using interference to make different combinations of wavelengths that is then sent through the gas that is being examined. By recording the intensity of the light exiting the gas, a spectrum will be obtained. This spectrum can then be Fourier transformed into a spectrum of the gases present in the gas examined. GC on the other hand uses the different chemical properties of the gases. By making the gas go through some (carefully chosen) liquid or solid in a tube, the time it takes for the gas to exit the tube will depend on the type of gas, thus a qualitative measurement of the gas phase can be obtained.

The other approach to study catalysis is to study the surface of the catalyst. This can be done using several methods. X-ray Photoelectron Spectroscopy (XPS) [3] or at higher pressures (typically around 1 mbar) High Pressure X-ray Photoelectron Spectroscopy (HPXPS) [4] are both techniques that show the chemical composition on the surface. Using x-rays, Einstein's photoelectric effect and a detector for both number as well as kinetic energy of the emitted electrons a spectrum will be obtained. This spectrum show the binding energy of the electrons (since the energy of the x-ray and the kinetic energy are both known) and each atom has a unique binding energy for each of its electronic states and the binding energy is affected by the chemical surrounding.

Not only the chemical composition on the surface has to be determined, the structure of the surface is also highly relevant, e.g. to determine active sites. This can be done by using Scanning Tunneling Microscopy (STM) [5] (p.96). STM uses a tip with a voltage on it that is placed close to the surface (without touching it). By being close to the surface some electrons may tunnel to the tip producing a current proportional to the number of tunneling electrons. This current increases when the distance

decreases between the tip and the surface. If the tip is moved and kept at the same height above the surface an image of the surface can be obtained since distance between tip and surface is known at all times due to the current going through the tip. Another way to study the structure of a surface is to use Surface X-Ray Diffraction (SXRD) [6]. By sending coherent photons with a precise and very short wavelength (around 0.1 nm) onto a surface a diffraction pattern can be seen by looking at different angles from the incident beam. This is due to that some of the photons are reflected on the first layer of atoms, some are reflected on the second and so on. For each layer of atoms that the photon passes before being reflected, it has traveled a certain distance longer (depending on surface structure and incident beam angle compared to surface layers) than the photons that was reflected at higher layers. This will give a diffraction pattern that is described by Bragg's law. This technique can be performed at atmospheric pressure since x-rays have no trouble traveling through a gas.

Most of these surface sensitive techniques require pressures at around 10^{-9} mbar (UHV), however, most of the reactions that are being studied, such as CO oxidation to CO_2 occurs at atmospheric pressure. This problem is usually referred to as the pressure gap and an intensive work within the catalysis community to bridge this gap. With the newer HPXPS, ambient STM and SXRD, pressures between 0.1 mbar and 1 bar can be used which provides results far closer to our everyday applications. Chmielowiec et al. used STM, in air at atmospheric pressure, in their study to determine that the catalytic activity was not dependent on spatial configuration for their di-iron hydrogenase complexes that were acting as catalysts. SXRD was used by Kaddouri, A. to determine which chemical states of the Cr atoms on their La_xCrO_y catalysts that were contributing to the catalytic effect at different temperature (between 300 and 800°C) at atmospheric pressure. Porsgaard et al. on the other hand used HPXPS at 0.25 mbar to determine how CO and O_2 react on the surface of a Pt catalyst.

These traditional methods rely on either measuring the gas phase products after the catalyst or conducting surface studies. Measurements on the gas phase lacks spatial resolution around the catalyst since the measurement is positioned at the outlet of the reactor and measures all gas that passes by the catalyst, or uses a probe to sample gas in a single point of the reactor. If the probe is used, not only is the measurement limited to one point (or to a scan over the interesting area that can take time), but the probe is also intrusive and may cause disturbance in the system, e.g. the flow field may change or heat may be transferred away.

Andersen et al. used a mass spectrometer to measure the reactivity of a catalyst while the temperature was varied which provided them with results about how the mole fractions of NH_3 , O_2 , H_2O and OH varied during the temperature ramp of the catalyst. That measurement did not have any detector that was looking inside the reactor so only one kind of data could be extracted. By instead combining this kind of measurement with an *in situ* technique, such as Laser Induced Fluorescence (LIF), a greater understanding of how the reaction with the catalyst works can be obtained. With LIF, an image that shows the mole fraction of the product in every point around the catalyst can be acquired and without interfering with the reaction, thus making it a powerful tool to use. Furthermore, LIF can be performed at high pressures and temperature as shown by e.g. Sadanandan et al. where LIF was used to track a mixing flow at 15 bar and temperatures above 1000 K [7].

Although using LIF in the IR region is a fairly new technique, it has been done successfully in the past [8, 9]. There are both benefits and drawbacks using IR LIF as will be discussed in further detail in

chapter 2.1 Laser Induced Fluorescence. The focus of this thesis is to characterize and see how a small reactor with optical access containing one or two catalysts behaves under different circumstances. The results obtained can be compared to results from other reactors, such as the one Zetterberg et al. had been using in their article [10], and be evaluated to see how well the reactor works.

A catalyst becomes active when it reaches a certain temperature. In this work the measurements were conducted by heating and then cooling the catalyst of interest, while using different detectors to try and gather useful information. The detectors used were, an MS that was examining the gas exiting the reactor, an IR camera detecting the LIF signal from the product gas CO₂ that was excited by a laser system and another IR camera detecting the temperature of the surface of the catalyst from above. There were also other detectors and indicators but their primary functions were to control flow, pressure and other parameters and not to gather results concerning catalysis.

By flowing different ratios of CO and O₂ through the reactor and using Ar as a bath gas to control the partial pressure of the other gases while maintaining a constant total pressure, the CO oxidation to CO₂ was followed as a function of temperatures using IRLIF. To make the LIF signal useful some preparatory measurements had to be done such as excitation scans to determine the best rotational line to excite and the delay time to for the detectors to maximize the signal-to-noise ratio.

2. Experimental methodology

The measurements conducted in this thesis collected data gathered from LIF signal, MS data from the entire reactor and temperature. Each of these sets of data had some field that they were superior to the other two but each of them also had drawbacks that could be compensated by looking at the other sets of data.

2.1 Laser Induced Fluorescence

Molecules, like atoms, contain energy levels. These energy levels are divided into three groups; electronic, vibrational and rotational levels. The electronic energy levels are built up by vibrational levels which in turn consist of rotational levels. For a given temperature, the distribution of molecules over these levels is always the same and follows a Boltzmann distribution. If the molecules from a given energy level are excited to a higher energy level, the molecules will quickly relax and emit radiation of some, most likely red-shifted, wavelength that is called fluorescence. The radiation is likely red-shifted because usually the molecule relaxes in several steps and for each of these steps the molecule loses some energy that is emitted as a photon this photon is red-shifted if the step is less than the whole way down to the ground state. After a molecule has relaxed ones, it has less energy than it received when it was excited and thus the remaining photons that can be emitted will also be red-shifted.

To excite the molecules from one particular energy level to another, a very specific amount of energy is needed. This energy is unique for that transition as well as for that species of molecules. This very specific energy can be transferred to the molecules by a laser that is tuned to the transition. Since lasers emit more or less monochromatic light, there are a high number of photons carrying the precise amount of energy needed (making an excitation more likely) and a transition can be chosen that is not overlapping with any other species in the system (to avoid interference). In this way, species specific measurements can be made. When the molecules relaxes the emitted fluorescence is detected, and it is thereby possible to perform the measurement non-intrusively, without disturbing the measurement object or region. By using a concave cylindrical lens ($f = -40$ mm) and a convex spherical lens ($f = 200$ mm) the laser beam can be converted into a laser sheet, covering a 2D plane inside the reactor. An image of the reactor can be seen in Figure 7. If the signal is imaged onto a 2D detector it is possible to collect a picture of the species distribution at a given moment, thus the locations of where the product is being formed can be seen. This technique is called Laser Induced Fluorescence (LIF) [11] or planar laser-induced fluorescence (PLIF) if performed in 2D. The possibility to non-intrusively measure in 2D with high spatial (down to 50 μm) and temporal resolution (typically on the order of ns) together with the fact that measurements can be performed *in situ*, are the main advantages and reasons to use laser diagnostics.

The decay time for ro-vibrational transitions is much longer than for electronic transitions. This increases the time that signal can be collected, from some ns to the order of 100 μs . The ro-vibrational transitions usually give fluorescence in the IR region which comes with a few complications such as the thermal background also emits photons in the IR region.

An upside of this technique is that the signal would be proportional to the mole fraction of target molecules, if compensated for temperature change due to constant pressure and volume, thus making relative measurements quite simple. However, due to effects like quenching and self-absorption, this is not always the case. Quenching, mostly originating from collisions, depends on the total pressure of the probed gas and decreases the signal with increasing pressure. Self-absorption also decreases the signal but is only dependent on the partial pressure of the target molecule.

Argon was used as a bath gas since it is completely inert. Using some other inert gas like N_2 could cause some disturbance in the system if the N_2 would dissociate at some surface with elevated temperature and then react with O_2 or something similar.

There are some problems that need to be dealt with before this technique can generate useful data. The number of molecules in a certain energy level is determined by the temperature of the gas, meaning that if the temperature changes, so does the signal strength which means that the signal could vary without there being a difference in mole fraction. The signal is also relative weak compared to the thermal background, originating from the Planck radiation, and is therefore hard to detect. This is a concern because we are working in the IR spectral regime (IRLIF) where Planck radiation is strong at moderate temperatures. Another problem is that the signal collected is over an interval of wavelengths and the camera is also sensitive to the light used by the laser ($2.3\mu\text{m}$). An interference filter that lets through light centered at $4.26\mu\text{m}$ with a FWHM of 150 nm was used to counteract some of these problems.

2.1.1 Background subtraction

Right after a laser pulse passes through the gas that was being probed, some of the targeted molecules are emitting light. There was also thermal background (Planck radiation) that covers the LIF signal due to it being stronger by some orders of magnitude than the LIF signal. Since the thermal background intensity is constant at constant temperature it can be compensated for by taking a second image close to the first but when all of the molecules have relaxed back to their ground state, and then the first image is subtracted by the second image. The temperature was more or less constant during this time since the images were taken with 50ms intervals and the temperature was usually increased by $0.5^\circ\text{C}/\text{s}$. The resulting image will only contain things that have changed between the images taken, such as LIF signal and non-constant noise. An example of this was made in Figure 1 and Figure 2 using partial pressure of 10 mbar CO_2 and 90 mbar Ar. A catalyst was placed within the reactor at the time of this measurement but since there were only Ar and CO_2 in the chamber, it was inactive.

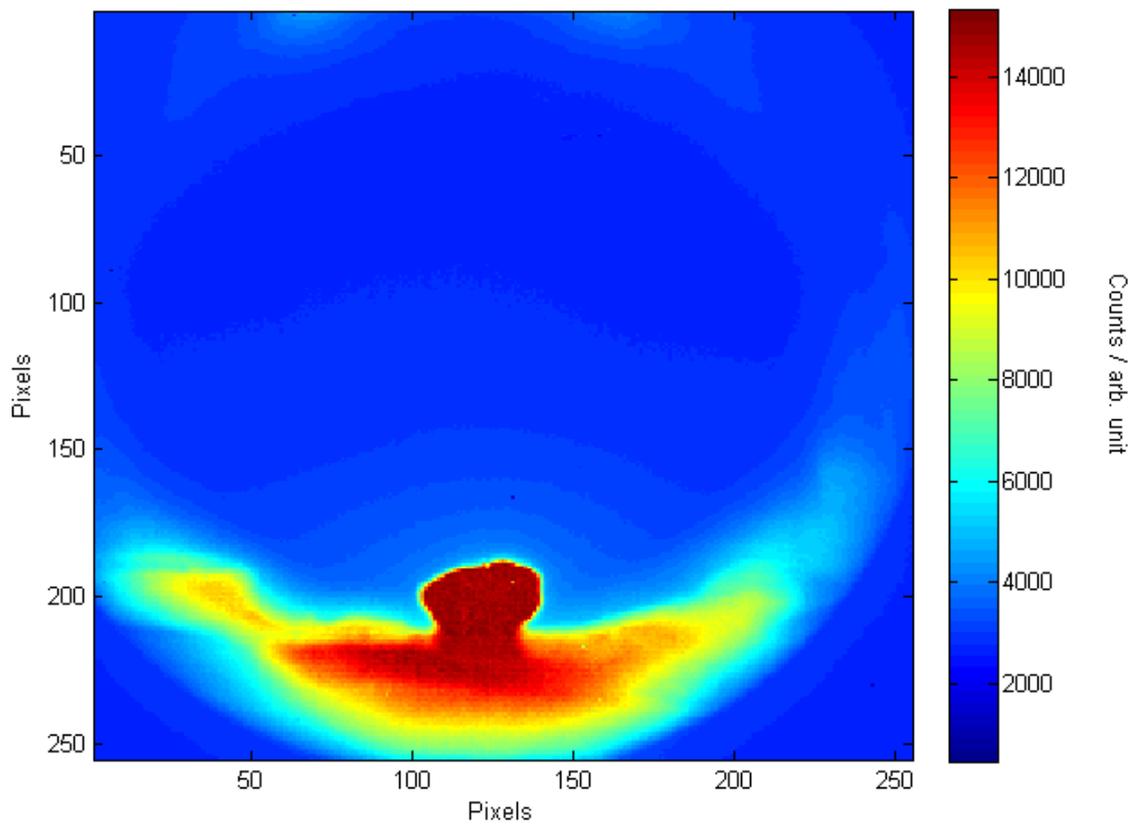


Figure 1. Raw single shot LIF image. LIF signal is not visible.

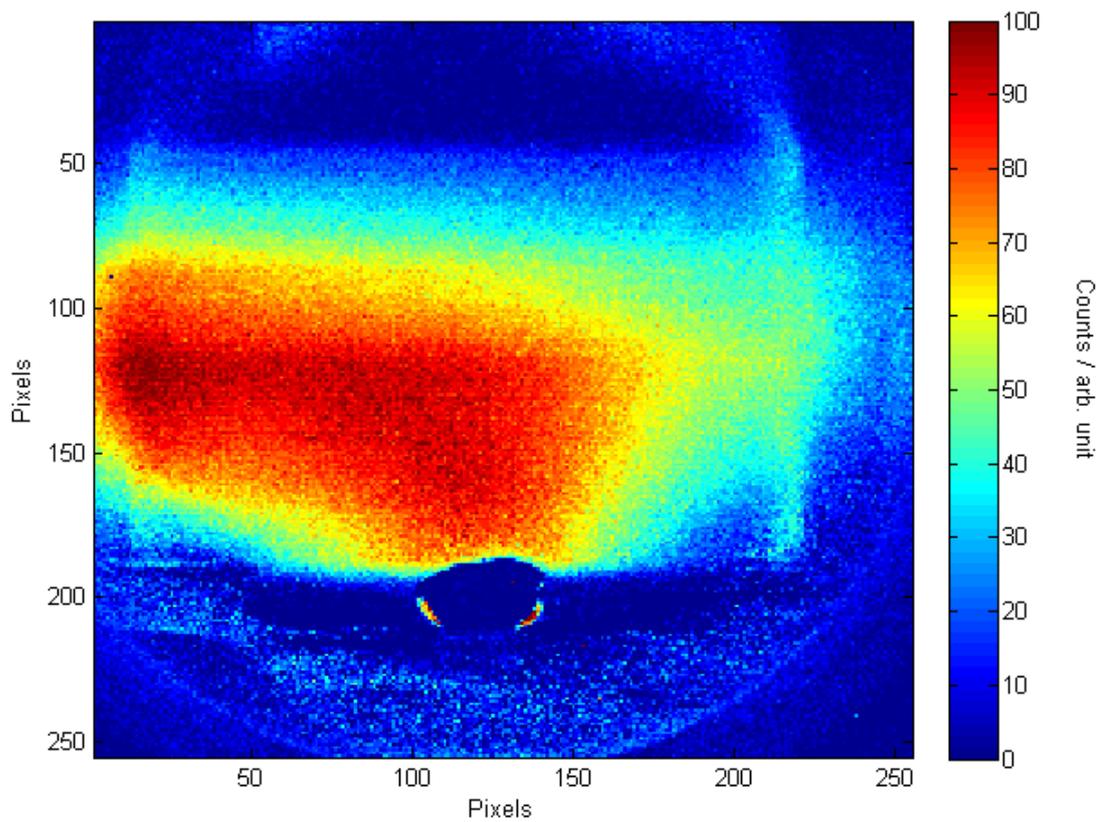


Figure 2. Single shot LIF image after background subtraction. LIF signal becomes clearly visible after background subtraction. The laser enters the reactor from the left and exits to the right.

2.2 Gas analysis

A catalyst speeds up reactions when it becomes active, thus higher concentration of the product gas should be detectable in the gas mixture exiting the reactor. By analyzing the gas, e.g. with a mass spectrometer, the activity of the catalyst can be determined with as a function of time. A drawback with analyzing the gas with MS is that there is a delay from when something happens in the reactor and until it is measured by the mass spectrometer, depending on the time it takes for the gas to travel from the sample to the MS, in our measurement this delay was 5 seconds. Another drawback is that there is no spatial resolution in the measurement, meaning that where the product is produced and how the flow looks inside the reactor remains unknown if only the gas is analyzed. In Figure 3 there is an example of how the mass spectrometer data looks when a catalyst becomes active. In the same figure there is also the detected LIF signal, which shows the delay between the two detectors. The LIF signal measures the change when the molecules have diffused a couple of millimeters above the catalyst while the MS measures the change first when the gas has left the reactor and travelled through some of the gas system. The data shows clearly when the catalyst became active by the mole fraction of the product (CO_2) increased while the mole fraction of the reactants (O_2 and CO) decreased. The delay between the LIF and the MS depends on the flow and pressure used for that particular measurement but should be within the same order of magnitude since all the measurements were conducted at total pressures and flows similar to each other.

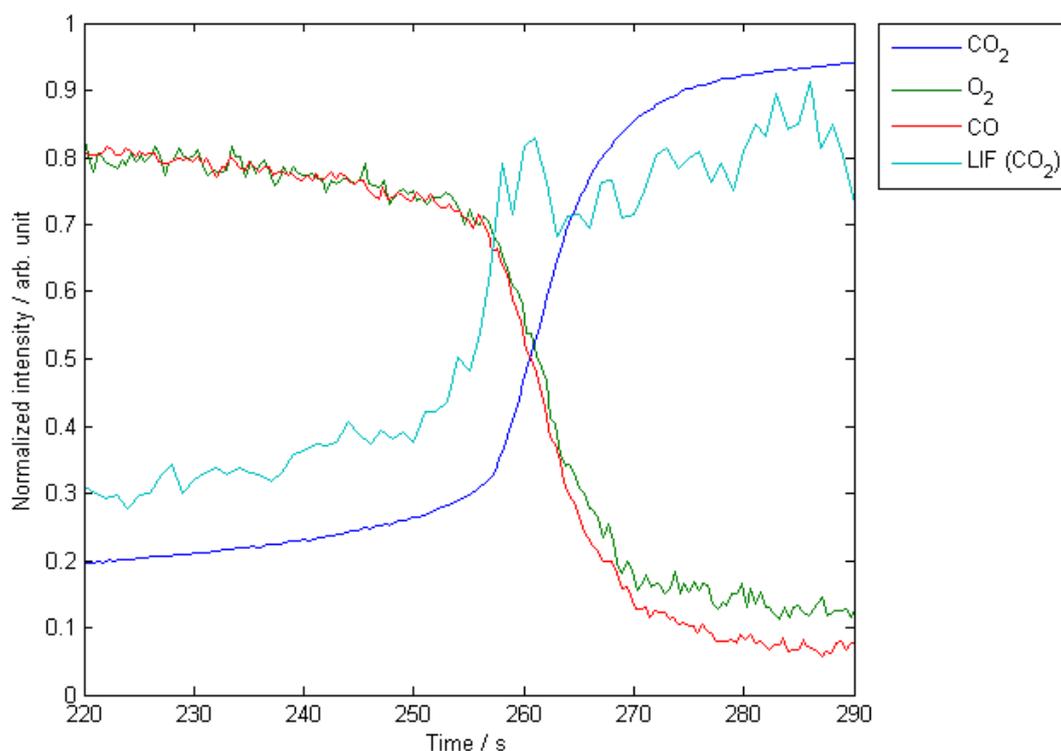


Figure 3. Zoomed in image of the mass spectrometer data synchronized with the LIF data at a time where a catalyst becomes active. The data in this figure was normalized. From the image it can be seen that the MS is measuring data with approximately 5s delay. The total pressure in this measurement was 100 mbar and the total flow was 216 ml/min.

The noise that can be seen for O_2 and CO data in Figure 3 is also present in the CO_2 data but the relative amplitude was lower. Notice that the data in Figure 3 shows the relative data for each gas

and not the measured ion current and if the noise's amplitude is not relative to the ion current for each gas but rather a constant background noise, the relative noise would be lower for gases with higher zero-level of ion current.

2.3 Temperature analysis

Chemical reactions are usually endo- or exothermic, both which affects the temperature of the surrounding molecules. If an active catalyst is present most of the reactants that reaches the surface will react with the aid of the catalyst, thus a temperature change can be detected on the catalyst. The measurement technique should be as non-intrusive as possible so that the reaction is not disturbed in any way. This can be accomplished by measuring the temperature with an IR-camera which detects the Planck radiation emitted from the catalyst and determines the temperature from that information.

Benefits with this technique are that instantaneous results with good temporal resolution (the maximum frame rate of the camera is 30 frames/s), can be obtained as well as a clear indication of the activity of the catalyst. The data collected only gives information about the temperature of the catalysts, which indicates that a reaction has occurred but the technique is still blind when it comes to determine which species are involved. Another problem is that the Planck radiation emitted from different materials at the same temperature is different. This depends on how good of a black body radiator the material is. A factor called emissivity can be used to compensate for this effect but the emissivity changes with temperature which makes it hard to use. All data collected here has had an emissivity calibrated for room temperature but not for the higher temperature and thus the temperature data for the catalysts gathered by the IR camera may have some off set. Still, good relative data (to itself) can be obtained, and gives a very good indication about the activity of the samples. An example of the temperature plotted against time can be seen in Figure 5. The value used for the emissivity for the catalyst was known from previous experiments not conducted in this thesis.

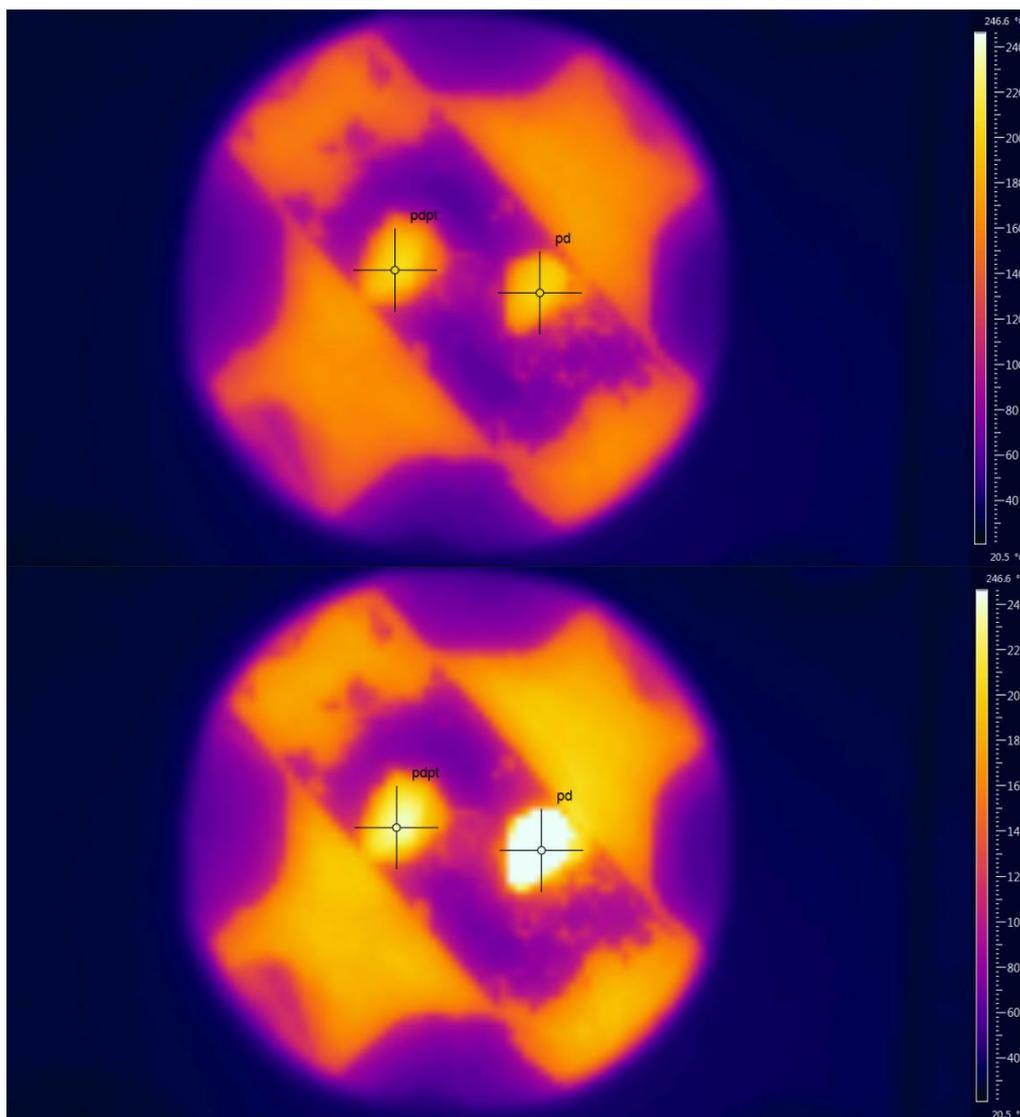


Figure 4. IR images showing the temperature in the reactor. The image is seen from above the chamber. The top image is taken 20 seconds before the bottom image, showing the change in temperature of one of the catalyst as it gets active. Notice that the image can only be used to visualize relative temperature change.

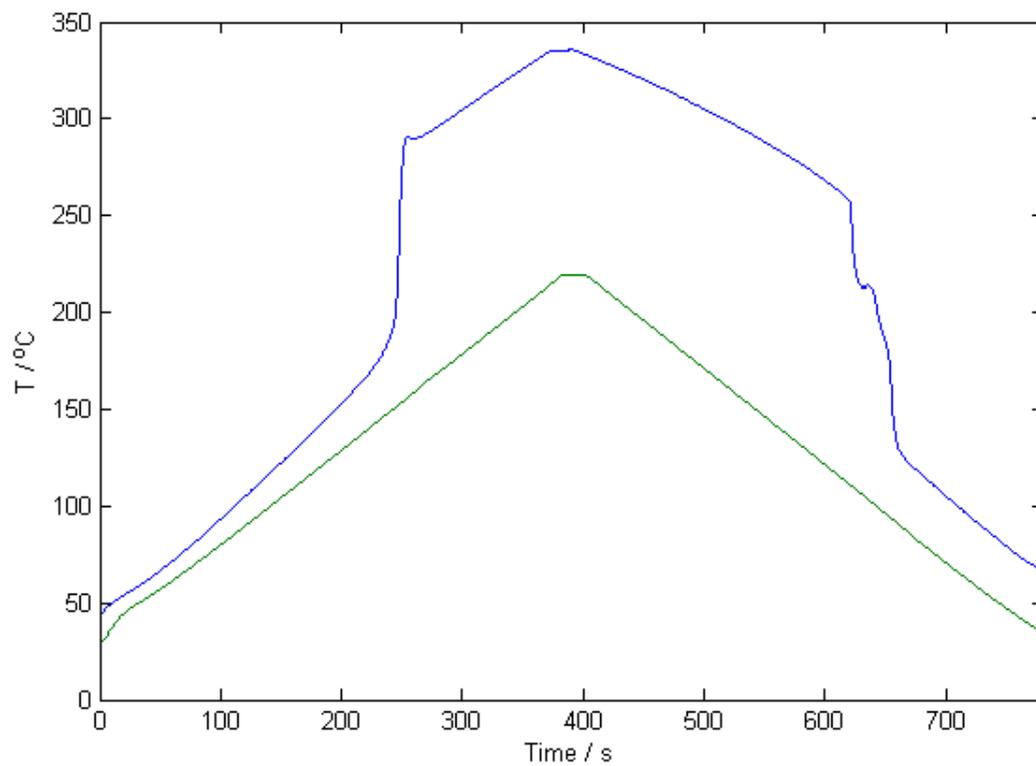


Figure 5. IR camera and thermocouple temperature curves. The blue curve shows the catalyst's temperature according to the IR camera and the green show the heating cross' temperature according to the thermocouple.

3. Experimental setup

The setup can be divided into four parts, reactor, laser, mass spectrometer and IR cameras. Each part has been described in the rest of this chapter. Figure 6 shows a schematic image of the setup.

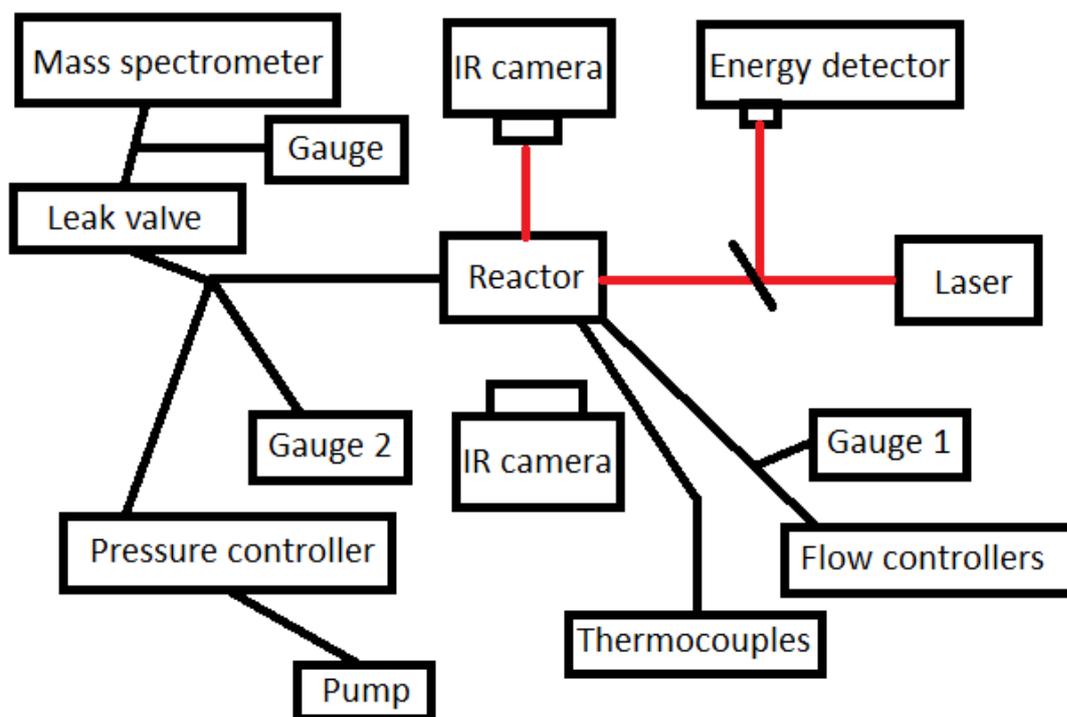


Figure 6. Schematic image of the experimental set up.

All the different analytics were computer controlled via a LabVIEW program to synchronize triggering and the acquired data. The LabVIEW program is described in Chapter 4. Regulation technique) and in Appendix C – In depth programming).

3.1 Reactor

The reactor was a 23 cm³ cube shaped chamber with CaF₂ windows on all four sides of it in the horizontal plane as well as a window on the top of it. The bottom part consists of a heating cross as well as a gas inlet and outlet.

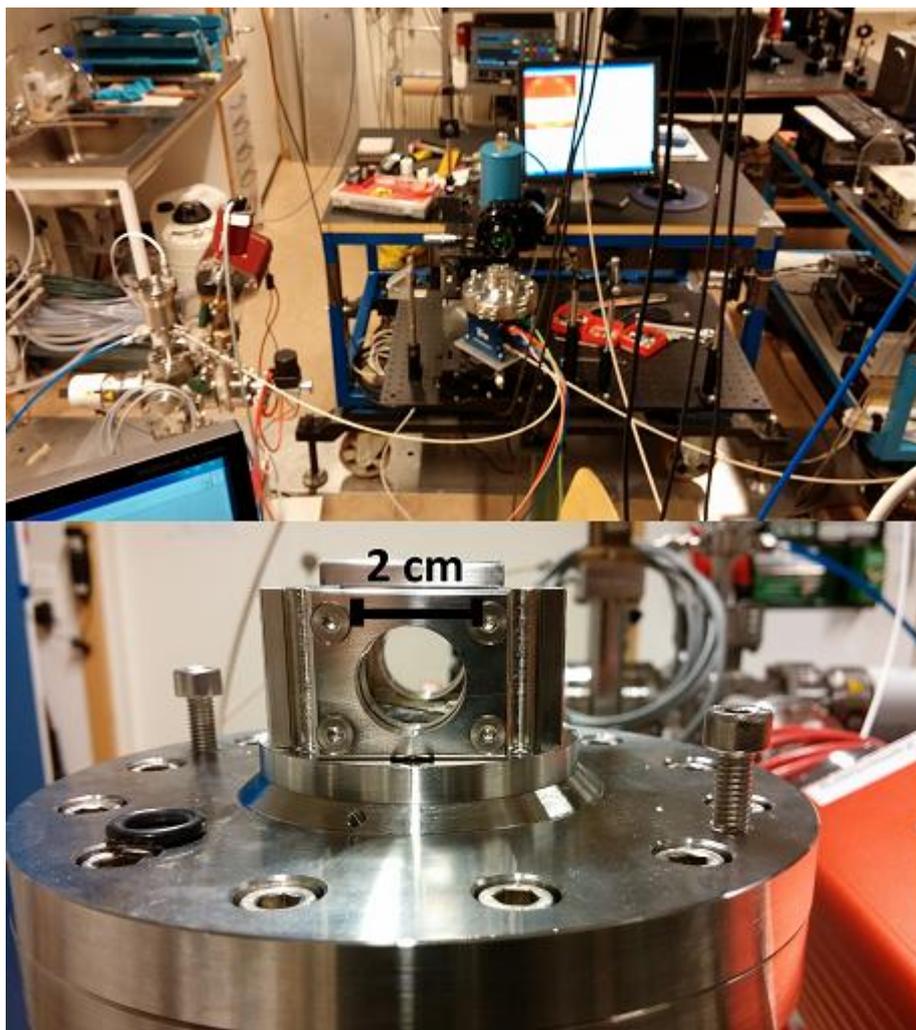


Figure 7. Images of the setup. The top image shows most of the gas system, the reactor and the IR camera used to detect LIF signal. The bottom image is a close up image of the reactor.

3.1.1 Heating cross

Heating the catalyst is the basis of these measurements. The heating cross consists of a boron nitride covered graphite wire and when a current is sent through the wire the temperature increases. The catalyst was placed on the heating cross and since the catalyst is small compared to the cross it should have the same temperature as the cross as long as no reaction takes place.

A thermocouple is connected to the heating cross to measure its temperature. This data is used to control the heating, which is explained in part 4.2 PID and does not contain any information regarding the activity of the catalyst. This temperature is recorded and can be used as an indication of what phase the measurement was in at that time. Also, the temperature is used to compensate the LIF signal for signal losses due to increased temperature.

3.1.2 Gas supply system

There was also a gas system for controlling the partial pressures and species inside the reactor. This system was made up by five mass flow controllers (MFC), Bronkhorst EL-FLOW; a pressure controller, Bronkhorst EL-Press; and a leak valve (Leiden Probe Microscopy), which leaked some gas in to a mass spectrometer so it could be analyzed.

The MFCs were calibrated for different gases and had different capacities. By multiplying the measured value with a correction factor (species specific) they could be used for any gas. The five MFCs used were calibrated for Ar, CO, O₂, Ar and H₂ respectively and could flow a maximum of 50, 200, 200, 200 and 50 ml/min respectively for the calibrated gas. Notice that there were two MFCs calibrated for Ar, one with a maximum capacity of 200 ml/min and one with 50 ml/min. The minimum the MFCs could reliably flow was 2% of the maximum value. The pressure controller could set the pressure to anything between 0.02 and 1 bar.

The gas system was connected to a vacuum pump which made the controllers able to work by creating a pressure drop at the end of the system (the pressure difference “drives” the flow).

3.2 Lasers

To be able to use LIF for CO₂ measurements and being able to do an excitation scan to find a suitable rotational line, a tunable laser is required. That laser in turn needs to be pumped by another laser. The pumping laser used was a Nd:YAG laser (Spectra Physics, PRO 290-10) operating at 10 Hz, providing a tunable dye laser (Sirah PRSC-D-18) with 690 mJ pulses at 532 nm (the 2nd harmonic of the Nd:YAG), which the dye laser turned into approximately 30 mJ pulses at a wavelength of 763.46 nm. These pulses were then mixed in a LiNbO₃ crystal with the fundamental of the Nd:YAG laser at 1064 nm, to form IR light at about 2.7 μm with pulse energy of around 5 mJ. Along with the lasers, some optics were used to shape a laser sheet that passed through the reactor. A schematic image of the lasers and optics used can be found in Figure 8.

The Q-switch of the YAG laser also sent trigger signals to a trigger box synchronizing all of the LIF measurement equipment.

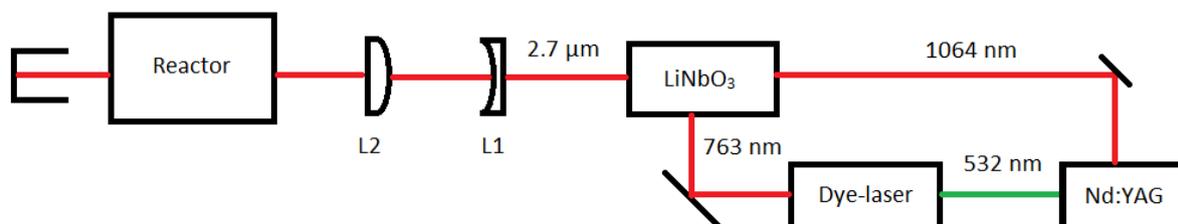


Figure 8. A schematic figure showing the laser set up and optics. L1 is a cylindrical lens with focal length -40 mm and L2 is a spherical lens with focal length 200 mm.

3.3 Mass spectrometer

After the reactor there was a leak valve that leaked some gas down to the mass spectrometer. All gas was not used because the mass spectrometer cannot handle pressures higher than 10⁻⁵ mbar and the measurements were never conducted at lower pressure than 10 mbar. The mass spectrometer (Pfeiffer PrismaPlus QME 220) analyzes the gas by looking at different mass/charge ratios, corresponding to different species in the gas. By ionizing the gas, it can measure an ion current for each mass that is proportional to the amount of molecules of the given mass. Measuring one mass

with the present MS takes roughly 0.1 seconds. Since the experiment only used gases with different masses each mass corresponded to one gas, e.g. mass 44 was CO₂ while mass 32 was O₂.

3.4 IR cameras

The setup contained two IR cameras. One of them was used to detect the LIF signal while the other one (FLIR P620) was mounted above the reactor looking down at the catalyst and heating cross. The camera looking from above measured temperature by looking at Planck radiation from the catalyst and heating cross, thus providing temperature data for the catalyst which could not be detected with the thermocouple placed on the heating cross.

The IR camera (Santa Barbara Focal Plane, SBF LP134) that detected the LIF signal was being triggered by a trigger box at 20Hz. The trigger box was in turn triggered by the Q-switch of the laser. This was done so that the first trigger pulse to the camera was shortly after the laser passed through the reactor. Thus the first image contained of the LIF signal. The second pulse came 50ms later when both fluorescence and laser had disappeared making it an image of the background noise which could be subtracted from the first image. An interference filter that lets through light centered at 4.26 μm with a FWHM of 150 nm was also placed in front of the camera.

4. Regulation technique

An important aspect of the measurement was to have everything synchronized with respect to time. Another important aspect was that every parameter should be easy to change and control both during and between measurements. For these two purposes a LabVIEW program was created so that the data collected would be saved into a common file and thus the data would have the same time stamps. The program also controlled several things, such as flow of gases, pressure, leak valve to the mass spectrometer and the temperature in the reactor.

4.1 Loop controlled program

The program that controlled all the equipment, except the IR cameras, the mass spectrometer and the laser, consisted of one initialize phase followed by a while loop that continued until the user pressed the STOP button.

During the initialize phase all parameters to the different equipment were read, instrument sessions were created and parts of the program (that the user chose before starting) was turned off, e.g. if the gauges were not connected the program would not run these parts if they were turned off.

Inside the while loop there was a built-in delay which made the loop take at least 250ms to execute which made sure that the program was running at 4Hz (this was changeable). The only thing that could make the loop take more than 250ms was if some part of the program took longer than 250ms to execute which, if everything was done correctly, should not happen. The importance of having 4Hz was that the density of measurement points would then be constant over the entire measurement. Higher update frequency of the measurements was not possible because the loop took on average 225ms to execute and to ensure that the delay time was never passed some margin had to be there as well since the execution time for everything else in the loop could vary by up to 40ms between iterations.

The buttons in the GUI worked so that if they were pressed the action they triggered usually occurred next iteration. The program is designed in such a way that most things can occur simultaneously which makes the order of execution for different parts of the program uncertain, although buttons were among the first functions to be executed each iteration.

4.2 PID

PID controller is an abbreviation of Proportional-Integral-Derivative controller. Several of the equipment used was controlled by a PID algorithm although only the leak valve and the temperature control had PID loops designed within LabVIEW, the flow and pressure controllers came with a built-in PID controller. The controller for the leak valve could be more correctly classified as a Proportional controller since it only checks the difference between target value (set point) and the measured value (process variable) and increases the output by taking this difference and multiplying it with a constant. This is repeated over and over which makes the gap between target and measured value

decrease over time. Although not as sophisticated as a complete PID controller it worked well and was enough for not making the leak valve open too much. The value for K_p was ~ 0.02 .

The temperature controller on the other hand used both the P and I in PID. The integral part of the PID saves the difference from previous iterations of the controller and modifies the output value provided by the proportional part based on how much the difference was in previous iterations. Using this kind of control proved insufficient since the temperature was oscillating back and forth (with an amplitude of up to 10 degrees Celsius) around the target temperature making the temperature changes becoming non-linear.

To make up for the lack of a good PID controller, a series of measurements was conducted to determine relation between current and temperature. The results of these measurements can be found in Figure 9. Only using the model determined by these measurements provided linear up and down ramps of temperature and an almost stable steady state but this was still not close enough to the target temperature, especially not at high (200-300 °C) temperatures.

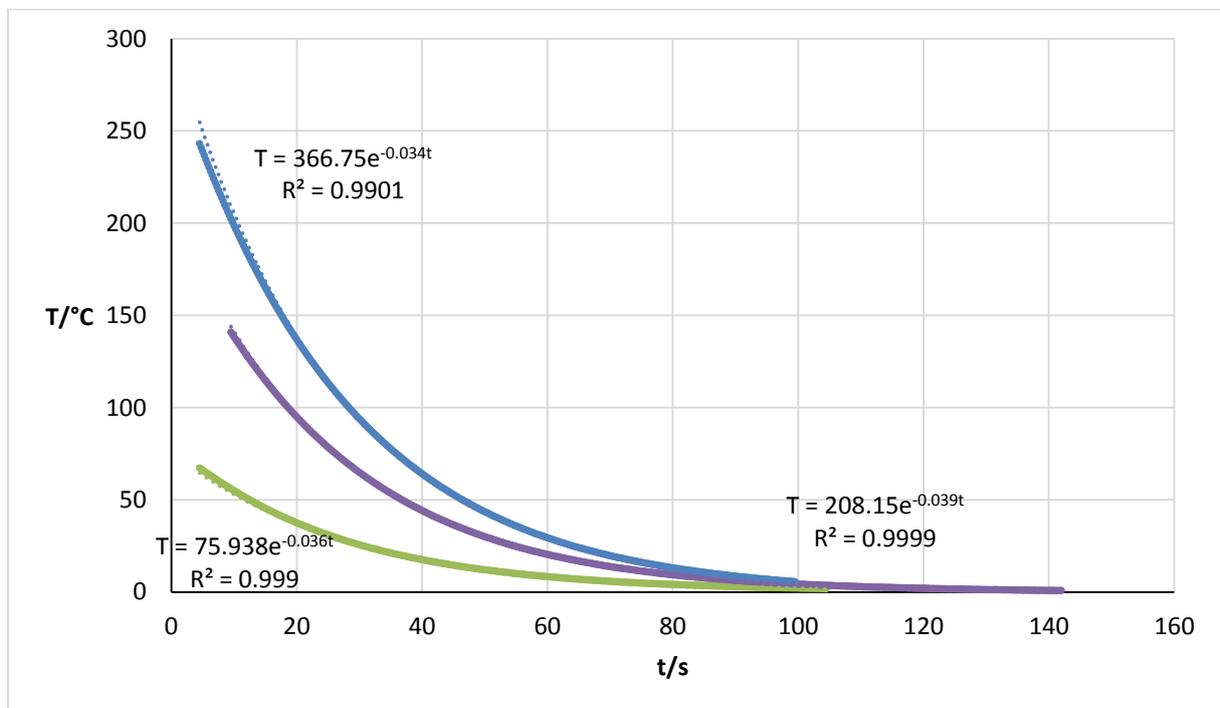


Figure 9. Cooling of the heating cross from different temperature with exponential functions based on least square method. Notice that the temperature axis was in Celsius minus room temperature.

Using a more general equation based on the ones found in Figure 9 where T is the temperature at a given time t and T_0 is the starting temperature,

$$T = T_0 e^{-0.039t} \quad (1)$$

Differentiating it with respect to time,

$$\frac{dT}{dt} = -0.039 \cdot T_0 e^{-0.039t} \quad (2)$$

And then substituting equation 1 into equation 2, equation 3 is obtained.

$$\frac{dT}{dt} = -0.039 \cdot T \quad (3)$$

The power P over a component in a direct current circuit follows equation 4 where R is the resistance of the material and I is the current.

$$P = RI^2 \quad (4)$$

Using the relation that power is the time derivative of energy and that the heat capacity, C , for a substance is constant for small changes in temperature, equation 5 is obtained.

$$P = \frac{dE}{dt} = \frac{d(T \cdot C)}{dt}$$

$$\frac{dT}{dt} \cdot C = RI^2 \quad (5)$$

Rewriting equation 5 results in equation 6.

$$\frac{dT}{dt} = \left(\frac{R}{C}\right) \cdot I^2 \quad (6)$$

To determine the approximated constant R/C , a measurement where a constant current was used until the system was in equilibrium. When the system was in equilibrium the temperature gain from equation 6 would be equal to the temperature loss in equation 3, forming equation 7.

$$\left(\frac{R}{C}\right) \cdot I^2 = 0.039 \cdot T \quad (7)$$

By inserting the current (0.75A) and the equilibrium temperature (93.7°C) into equation 7 the constant could be determined to 6.50.

The total temperature change is obtained by adding the temperature loss with the temperature gain, which means adding equation 3 and 6, forming equation 8.

$$\frac{dT}{dt} = -0.039 \cdot T + 6.50 \cdot I^2 \quad (8)$$

Since an expression for the current required to heat the sample at a known temperature and a known temperature change was the goal for this model, rewriting equation 8 by isolating the current results in equation 9 that can be used in the program.

$$I = \sqrt{\frac{\frac{dT}{dt} + 0.039 T}{6.50}} \quad (9)$$

Since the PID controller was really good at oscillating around the target temperature and the modeled controller was really steady, a hybrid controller was created which took 80 % of the output value from the steady, modeled, controller and added it to 20 % of the oscillating, PID, controller. This hybrid controller was later used during the experiments since it was never more than one

degree Celsius away from the target temperature (except when the ramp up stopped, then it could overshoot the temperature with approximately the value that the temperature had been increased with each second during the ramp up, usually around half a degree).

The values for K_p and T_I was different for different parts of the measurement. For the first half of the ramps up or down they were 4 and 0.2 respectively and the second half were they 4 and 0.6. During steady states were they 4 and 1 respectively.

5. Preparatory measurements

Before measurements with catalysts could be done the LIF signal dependence on different parameters was first investigated since many of these could change during a catalytic measurement. The fluorescence signal is dependent on the number density of target molecules (CO_2 in our experiment) and the population at the chosen energy level which the molecules were excited to produce the signal. Since the catalytic measurements were conducted by ramping up and ramping down temperature in the reactor and both these two parameters depends on temperature, measurements to compensate for the temperature had to be conducted or the relative data would be destroyed by changing temperature. Another important aspect is signal-to-noise ratio. By using different delay and integration times for the detector used to detect the LIF signal a higher signal-to-noise ratio can be obtained and thus better results.

The laser enters the reactor from the left and due to absorption of the LIF signal by the CO_2 molecules; the intensity would be stronger on the left side of the reactor compared to the right side. To compensate for this effect, before and after every measurement 250 images were taken when the reactor was filled with a total pressure of 100 mbar and partial pressure of 0.5 mbar CO_2 and 99.5 mbar Ar. These images were then averaged and normalized, and the measurement images were then divided by these images to remove the effect of absorption. This compensation was conducted at similar CO_2 concentrations as for the catalytic measurements and small variations would give a similar absorption behavior in the reactor. When a catalytic measurement was conducted, the concentration of CO_2 was close to zero the whole time until some temperature when the sample became active and after that point the concentration was almost constant again. Because of that behavior, compensation like the one described would be enough to get comparable results.

These measurements were conducted without catalyst and with constant partial pressures and flow of CO_2 and Ar, and at constant temperature.

5.1 Excitation scan

To be able to use LIF the drawbacks of the technique must be diminished. The problem that the number of molecules in an energy level changes with temperature can be solved by choosing a transition which gives roughly the same signal at different temperatures. This can also be compensated for by simulating the population in the chosen energy level, from which the molecules are excited, at different temperatures and then divide the signal with this number. If this is done the transition should be one that gives high signal at preferably the entire temperature range but most importantly in the region where the catalysts becomes active (at around 200°C). Finding such a transition can be done through excitation scans at different temperatures and choosing the peak that is amongst the highest at all the temperatures.

An excitation scan is performed by using a tunable laser, a detector and with a constant concentration of the molecule which is going to be examined in the reactor. The laser wavelength is slowly changed over a wavelength interval and for every change of wavelength the signal is collected until a spectrum showing different transitions and the corresponding signal strengths is obtained.

The scans conducted were at 23°C, 200°C and 300°C and can be seen in Figure 10, Figure 11 and Figure 12. The peaks could be identified by comparing to a simulated spectrum using input data from the HITRAN database [12], shown in Figure 13. The peak that was the most constant and with a high intensity for these temperatures was the peak 18 in the P-branch and that peak was thus chosen as the transition the laser was tuned to for the measurements. This corresponded to laser wavelength of around 2.7 μm .

The peaks' names come from what rotational quantum number the ground state of the transition had, e.g. peak 18 in the P-branch was excited from vibrational level $v' = 0$ and with rotational quantum number $j = 18$ to $v'' = 1$ and $j = 17$. Q-branch works similar but the j quantum number is not changed. The R-branch (that can be seen in Figure 10, Figure 11 and Figure 12 as the last three peaks to the right) is the same as the other two branches except that the j quantum number is increased by one.

There were new small peaks for the scans conducted at 200°C and 300°C. These peaks were caused by molecules that have populated another vibrational level than the one that most of them were in at room temperature. These peaks were ignored since they would generate close to no signal at room temperature since they were not distinguishable from the background.

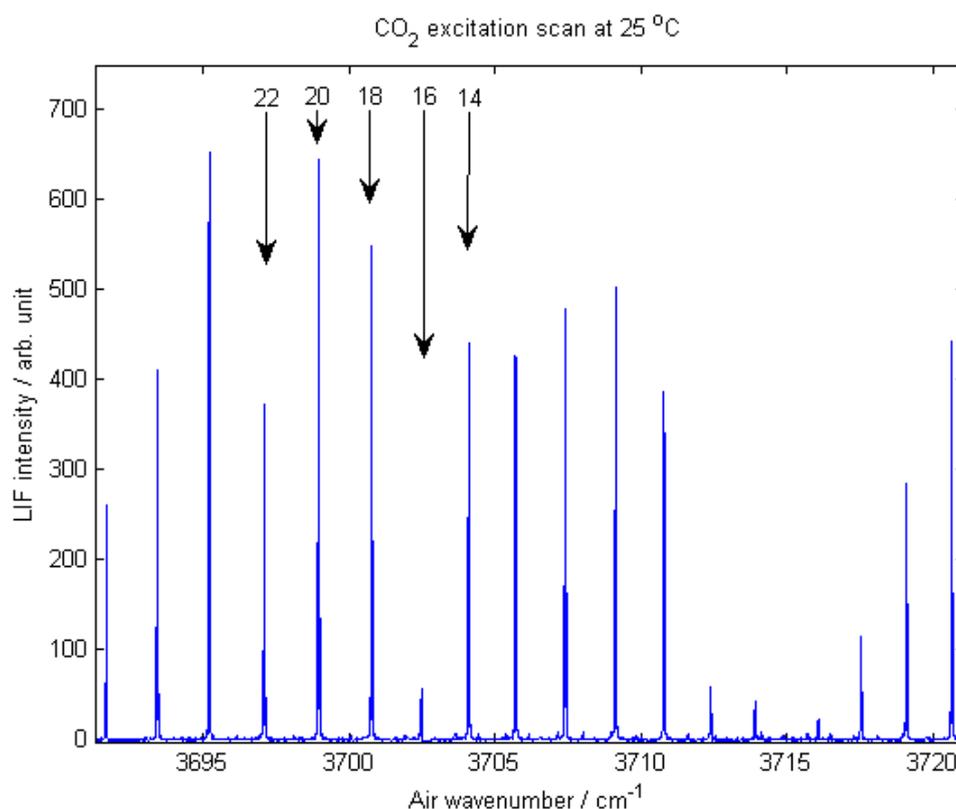


Figure 10. Excitation scan at 25°C. Some of the interesting P-branch lines were marked.

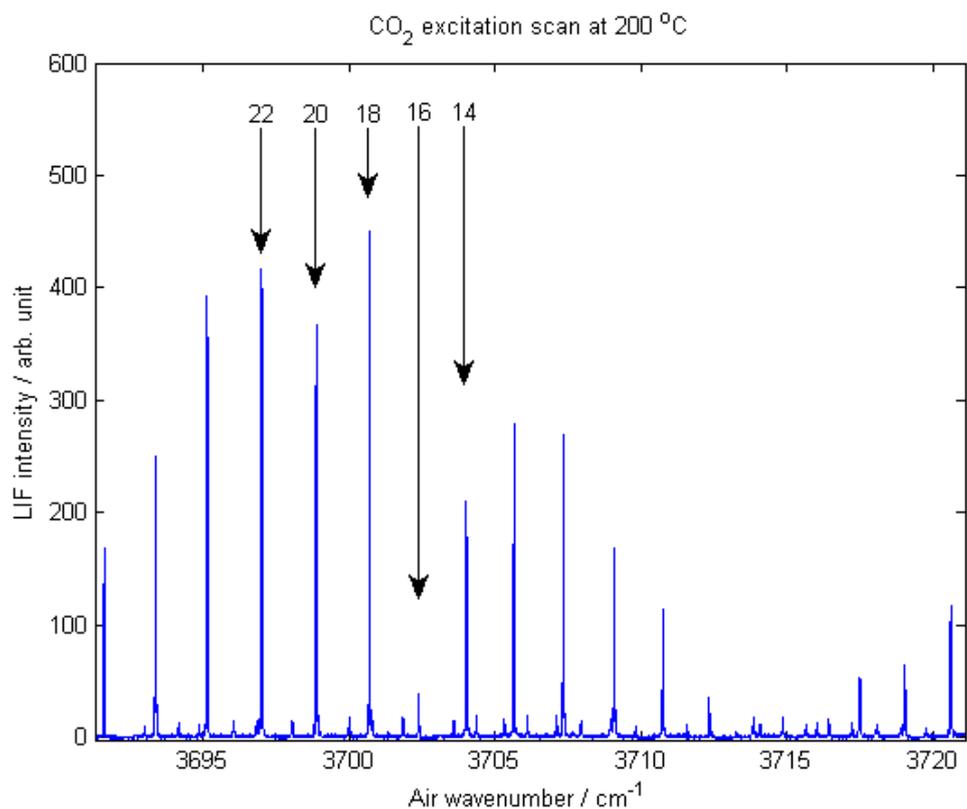


Figure 11. Excitation scan at 200°C. Some of the interesting P-branch lines were marked. Small peaks between the larger ones were due to population in higher vibrational levels.

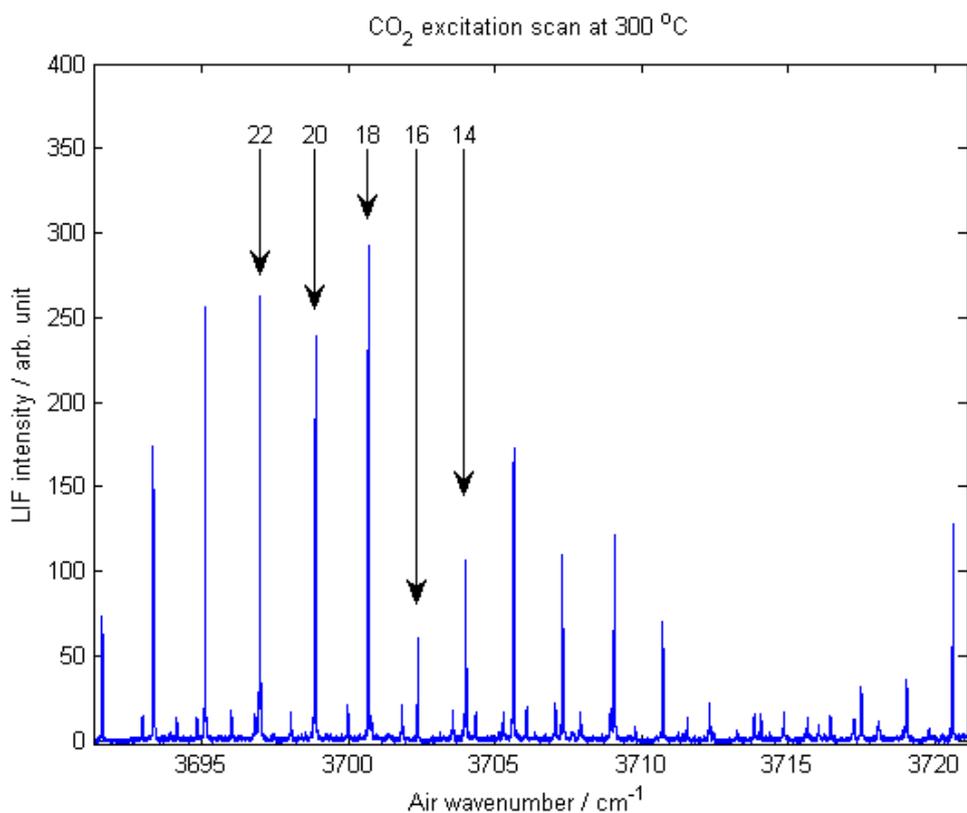


Figure 12. Excitation scan at 200°C. Some of the interesting P-branch lines were marked. Small peaks between the larger ones were due to population in higher vibrational levels.

The peak 16 in Figure 10, Figure 11 and Figure 12 is weaker than it is supposed to be. By simulating an absorption spectrum for water at the relevant wavenumber interval it can be seen that one of the absorption peaks coincides with peak number 16 in our excitation scans. By simulating an excitation scan and assuming a finite amount of water in the air, a qualitative spectrum similar to our observations can be simulated. The result is presented in Figure 13.

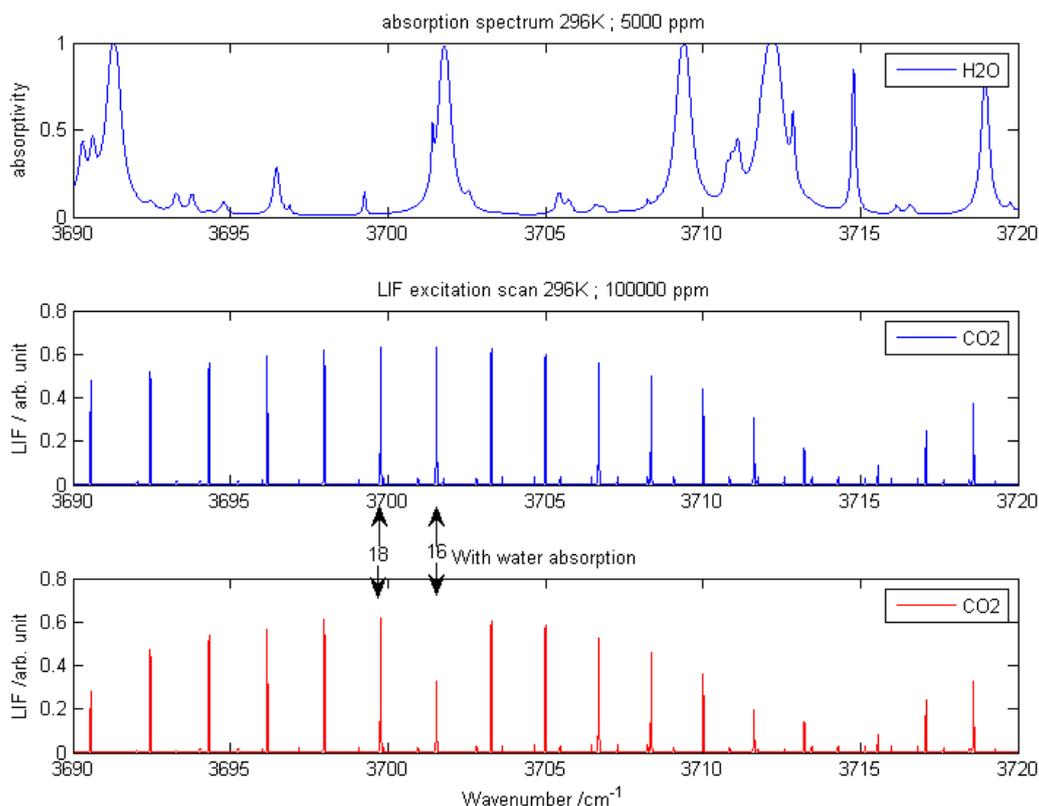


Figure 13. Simulated absorption spectrum for water and two LIF excitation scans. The last graph shows the LIF excitation scan if the water absorption was taken into account. The lines 18 and 16 from the P-branch were marked. The simulated values use input data from the HITRAN database [12].

There were other lines that differ some from the simulated excitation scan as well but those differences were most likely caused by fluctuations in laser energy during the scans.

5.2 Delay time

When constant noise, such as detector noise and thermal background, has been removed the resulting image still has some noise left caused by the laser. Reflection and heating caused by the laser are sources of detectable light that were unwanted but only present while the laser sheet was in the reactor and shortly after. To remove this source of error a delay time starting from the laser trigger pulse could be used so the first image was taken at a (short) fixed time after the laser sheet was gone. Having a short delay time increases the signal intensity but at the same time allows more residual effects of the laser to be captured. Having a long delay time will on the other hand capture no residual effects of the laser (except for LIF signal) but the signal intensity will be much weaker since the molecules relax once the laser stops exciting them. Although, according to the

measurement found in Figure 14, this was not quite true in our case. Most likely the decay of the signal is so slow that it is almost constant over the time interval that was examined which means that most of the delay times would probably work just as well as the one we chose (as long as it is not too short) but this was not known before the measurements were conducted.

By testing different delay times, the value that gave a high signal intensity and low noise was chosen. The tested times were 0, 1, 2, 5, 10, 15, 20 and 30 μs . After evaluating the results, which are presented in Figure 14, 10 μs was chosen as the delay time. For these measurements integration time of 15 μs , total pressure of 100 mbar and a partial pressure of 10 mbar CO_2 were used. It was also conducted at room temperature (23°C).

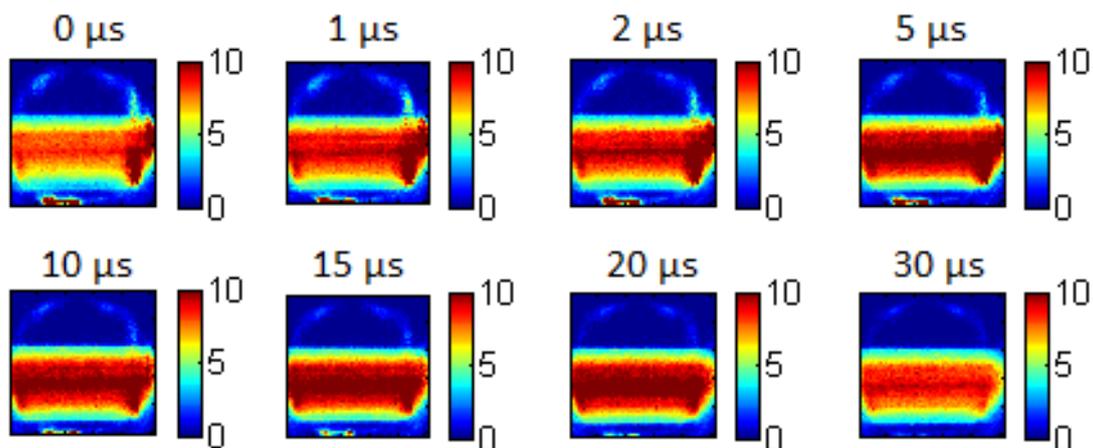


Figure 14. LIF signal with different delay time. The times used were 0, 1, 2, 5, 10, 15, 20 and 30 μs .

5.3 Integration time

The time that the detector collects signal is called integration time. The longer the detector is running, the more signal is collected. At the same time more noise is also collected. Since the noise is more or less constant while the signal decays, a short integration time would be preferable. Another aspect is that the detector can be saturated by the thermal background if a too long integration time is used which would ruin the measurement. Although the time has to be long enough so that there is enough signal detected. A series of tests with different integration times were conducted. The times tested were 5, 10, 15, 20, 25 and 30 μs . These measurements used a delay time of 10 μs , total pressure of 100 mbar, and a partial pressure of 10 mbar CO_2 . The measurements were conducted at 250°C and are shown in Figure 15. The signal intensity was enough in 20, 25 and 30 and because of the trade-off between saturation, signal-to-noise ratio and signal, 20 μs was chosen since a shorter integration time with enough signal was preferred over a longer integration time as discussed before.

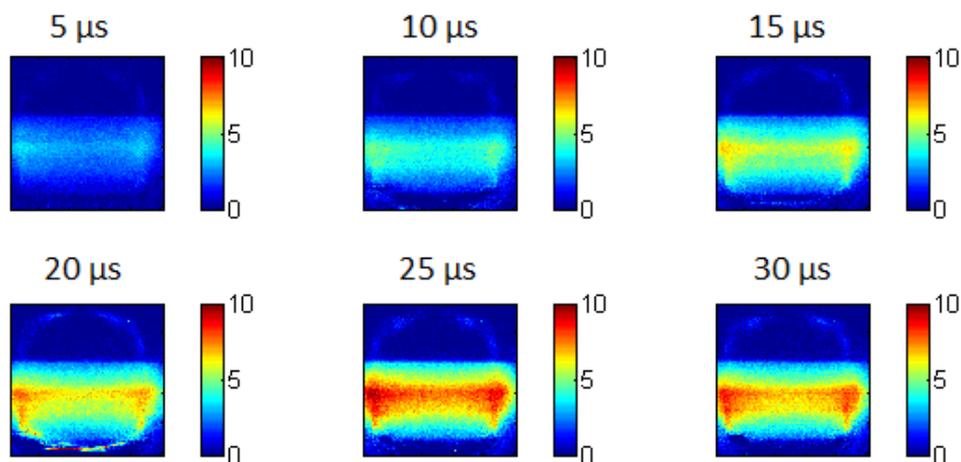


Figure 15. LIF signal with different integration times. The times used were 5, 10, 15, 20, 25 and 30 μs .

5.4 LIF signal dependence on CO_2 partial pressure

A total pressure of 500 mbar was kept constant for these measurements while the partial pressures of CO_2 and Ar were changed. Delay time of 10 μs and integration time of 20 μs were used as previously discussed. Figure 16 shows how the collected fluorescence signal depends on partial pressure of CO_2 . Something to note is that the first half of the figure shows a linear behavior but the second half shows that the signal becomes less proportional with increased partial pressure. This was measured so that compensation could be made if quantitative data would be required. As long as each partial pressure corresponds to one value of LIF signal, this could be done.

In theory the signal should have a linear relation with the partial pressure of CO_2 but due to the effect of self-absorption, this is not the case. Self-absorption occurs due to the CO_2 molecules can be excited with photons of the same wavelength as they emit when LIF is used. If a molecule absorbs one of the fluorescence photons it can either relax some other way and send out photons of a different wavelength or send out a similar photon as the fluorescence photons but in a different direction. In both cases the photon will never hit the detector and there will be some loss of signal. The probability that this occurs increases with the number of CO_2 molecules in the photons path to the detector. In the catalytic measurements that was performed, the partial pressure of CO were almost always 12.5 mbar, thus the maximum partial pressure possible of CO_2 to be formed in the reactor was 12.5 mbar which is within the range of the curve found in Figure 16 and can thus be used for qualitative measurements without any problem.

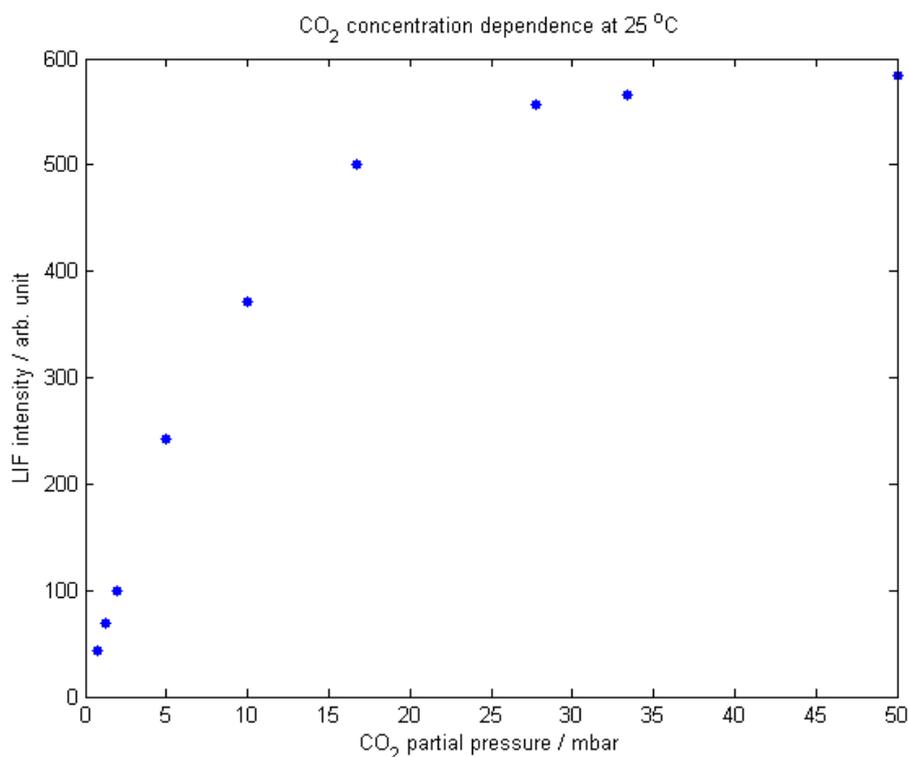


Figure 16. LIF signal dependence on partial pressure of CO₂. For lower pressure there is a linear dependence which is less and less accurate with higher pressures.

5.5 Temperature compensation

The population of an energy level changes with temperature, since the LIF signal is proportional to the population the same goes for that. The signal had to be compensated for that and using data from the HITRAN database [12]. A simulated function for the population could be made and then divided with the measured data to remove the effect of decreasing LIF signal due to temperature change.

There was also the effect as a result of ideal gas law. Since the pressure and volume was kept constant in the chamber, the amount of molecules decreased leading to decrease in signal. Since it was mole fraction or partial pressure that was the goal to measure with the LIF signal, this effect had to be compensated for as well in a similar manor to the population change. Figure 17 shows LIF signal before and after compensation as well as corresponding MS data. Notice how the MS data matches the LIF signal better after compensation since the mole fraction of CO₂ should be constant or "flat" while the catalyst is active.

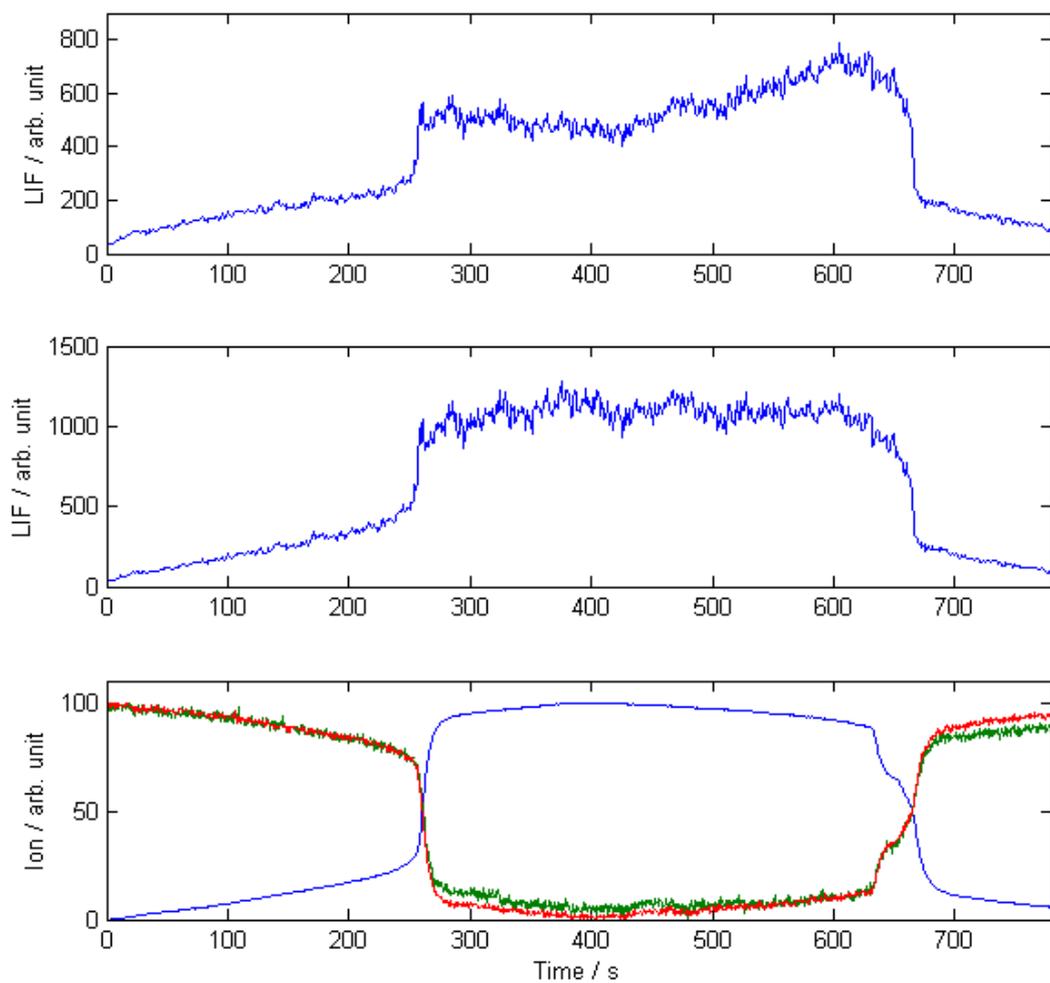


Figure 17. Top graph shows LIF signal before temperature compensation. Middle graph shows LIF signal after compensation. Bottom graph shows MS data.

6. Catalytic measurements

Using data collected during measurements in Chapter 5. Preparatory measurements, flows and pressures were chosen to give comparable results. For these measurements CO, O₂ and Ar were used and the temperature was ramped up and then down again between different temperatures depending on how much flow was used, type of catalyst and pressure.

6.1 One catalyst measurements

To see how a catalyst would behave in the reactor, what flows would work well and similar things, the first measurements were conducted with only one catalyst in the reactor. Figure 18 shows the results from LIF, mass spectrometer, thermocouples and IR-camera. The catalyst becomes active at around 175°C, which can be seen on the LIF signal and mass spectrometer graphs at around 220 seconds. Notice that the mass spectrometer graph is slightly delayed. This was due to that the gases had to be transported away from the reactor over to the mass spectrometer before the data could be collected. That means there was always (approximately) 5 seconds delay from the LIF signal showing a change until the mass spectrometer was showing the same change. The delay varied with pressure and flow through the reactor.

The measurements with one catalyst were conducted with a 2% Pd, 98% CeO_x catalyst. The total pressure was constant at 500 mbar but different partial pressures were examined as well as different flows. The temperature ramp was also varied.

For the measurement in Figure 18, the temperature was ramped from 30 to 220°C and then down again with a speed of 0.5°C/s. The flows were 27, 27 and 162 ml/min for CO, O₂ and Ar respectively. The partial pressures were then 62.5 mbar, 62.5 mbar and 375 mbar for the gases. The laser wavelength for this measurement was approximately 2.7 μm. The integration time of the detector was 20 μs and the delay time was 10 μs with respect to the Q-switch. The images in Figure 18 and Figure 19 are both averaged over ten shots after background subtraction.

The LIF signal in both Figure 18 and Figure 19 have noise in them making the signal go up and down with each measurement point. But the signal in Figure 19 also has some sudden drops in intensity between 300 and 600 s into the measurement. This is most likely caused by the diode-seeding of the Nd:YAG laser, making the Nd:YAG laser output have a broader wavelength interval thus the energy of the wanted wavelength decreased and so did the signal. The diode seeding went unstable from time to time but quickly regained normal capacity again.

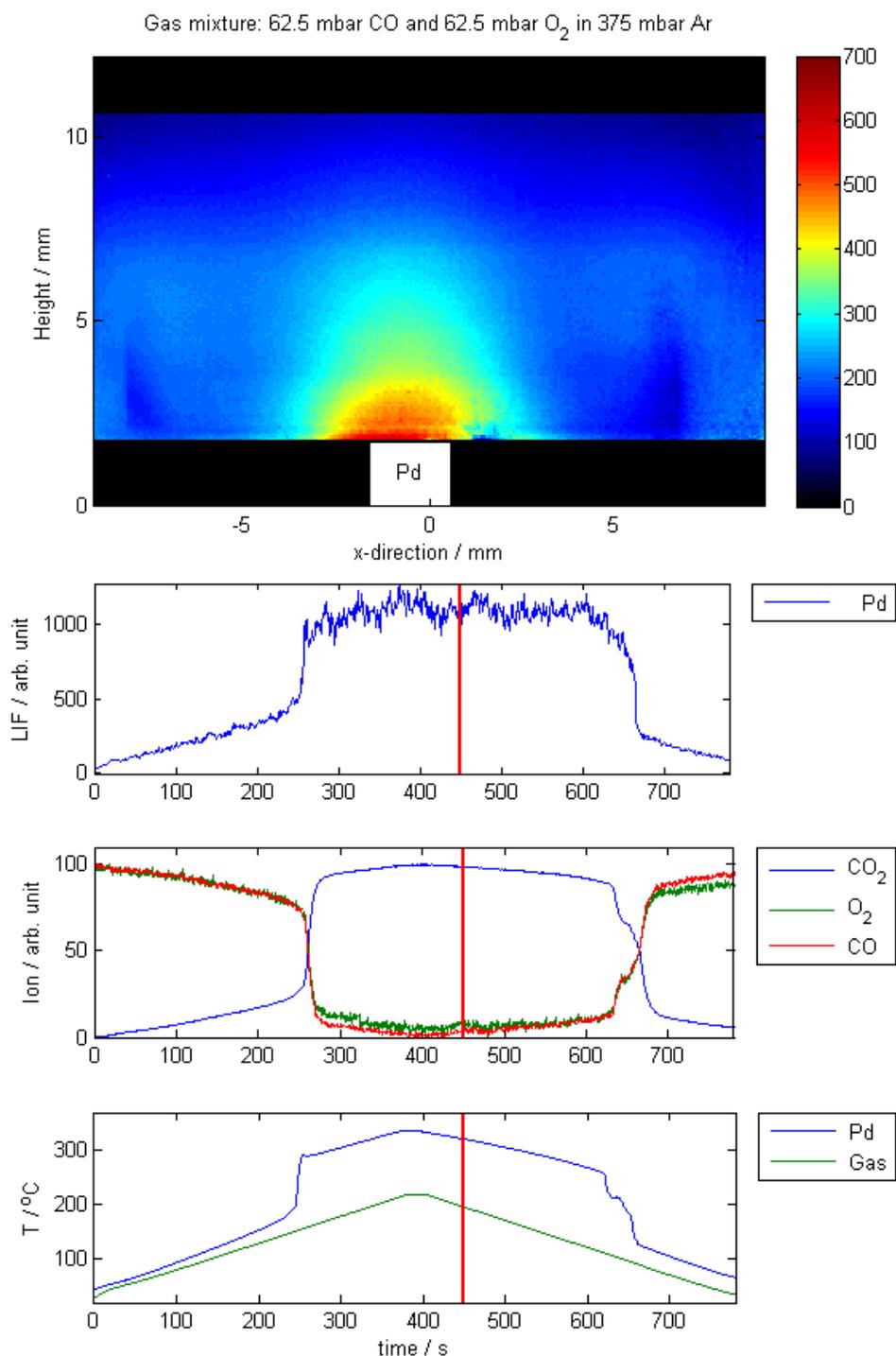


Figure 18. Top image show the LIF signal for a one catalyst measurement. Below that the LIF signal, mass spectrometer and temperature data were plotted against a common time axis. The red line shows at what time during the measurement the image was taken. The MS data has been normalized and the LIF signal has been compensated for temperature variations.

The mass spectrometer data sometimes varied at random as well as there could be a trend over 10 minutes where the gas concentration was decreasing slightly. These effects were visible for all of the gases at the same time, but more prominent for some of them. Because of this the data had to be normalized compared to the Ar data to reduce some of that noise and to give a clearer image of what

happened. The data was also normalized to itself afterwards so that clear species variations could be seen.

Since the population in each energy level change with temperature, the LIF signal will also change. For the chosen transition (line 18 of the P-branch) the population would decrease, making the signal weaker with increasing temperature. Another factor to consider was that since there was a constant pressure and a constant volume, the density of molecules would also decrease with increasing temperature, decreasing the LIF signal once again. These two effects were compensated for in the displayed result in Figure 18 and Figure 19.

6.2 Two catalysts measurements

One of the strengths of using all of the three detectors in our measurements was that more than one catalyst could be studied at the same time, thus the catalysts would have close to the same conditions and the data would be easier to compare. In these measurements two catalysts were examined, 2% Pd in CeO_x and 1% Pd, 2% Pt in CeO_x. The measurements were conducted in similar fashion to the measurements for one catalyst except that now data was collected for both the catalysts. Figure 19 shows data from a measurement with the two catalysts. The data shows that the catalysts behave differently and that the 2% Pd (right sample in the figure) became active at a lower temperature (170°C) than the 1% Pd, 2% Pt (left sample). The left sample was producing CO₂ already at 50°C but had an increase in activity at 230°C. The first peak was clearly visible on the MS as well as on the LIF signal. Although the MS cannot tell us which catalyst became active the LIF signal can do that. The second peak cannot really be distinguished on the LIF chart but can be seen in both the MS and the temperature chart. Once again the MS only gives an indication that something happened while the IR camera measuring the temperature shows what happened. The LIF signal indicates that both samples were active at around 350 seconds but the second peak (for the PtPd catalyst) was missing, it looked more like a linear increase for the entire temperature ramp.

For the measurement in Figure 19 the temperature was ramped from 50 to 250°C and then down again with a speed of 0.5°C/s. The flows were 27, 27 and 162 ml/min for CO, O₂ and Ar respectively. The partial pressures were 12.5 mbar, 12.5 mbar and 75 mbar for the gases. The integration time was 20 μs and the delay time was 10 μs.

The flow in this experiment was enough to replace all the gas in the reactor every 6.4s. Since the images that can be seen in Figure 18 and Figure 19 are averaged over one second the effect of the flow in these two cases would not be that high. In another experiment (that is not included in the thesis) where the total flow was 500 ml/min instead of 216 ml/min some effect on the CO₂ cloud around the catalyst could be seen. The cloud was slightly shifted to the left; the effect was more prominent at the upper parts of the reactor.

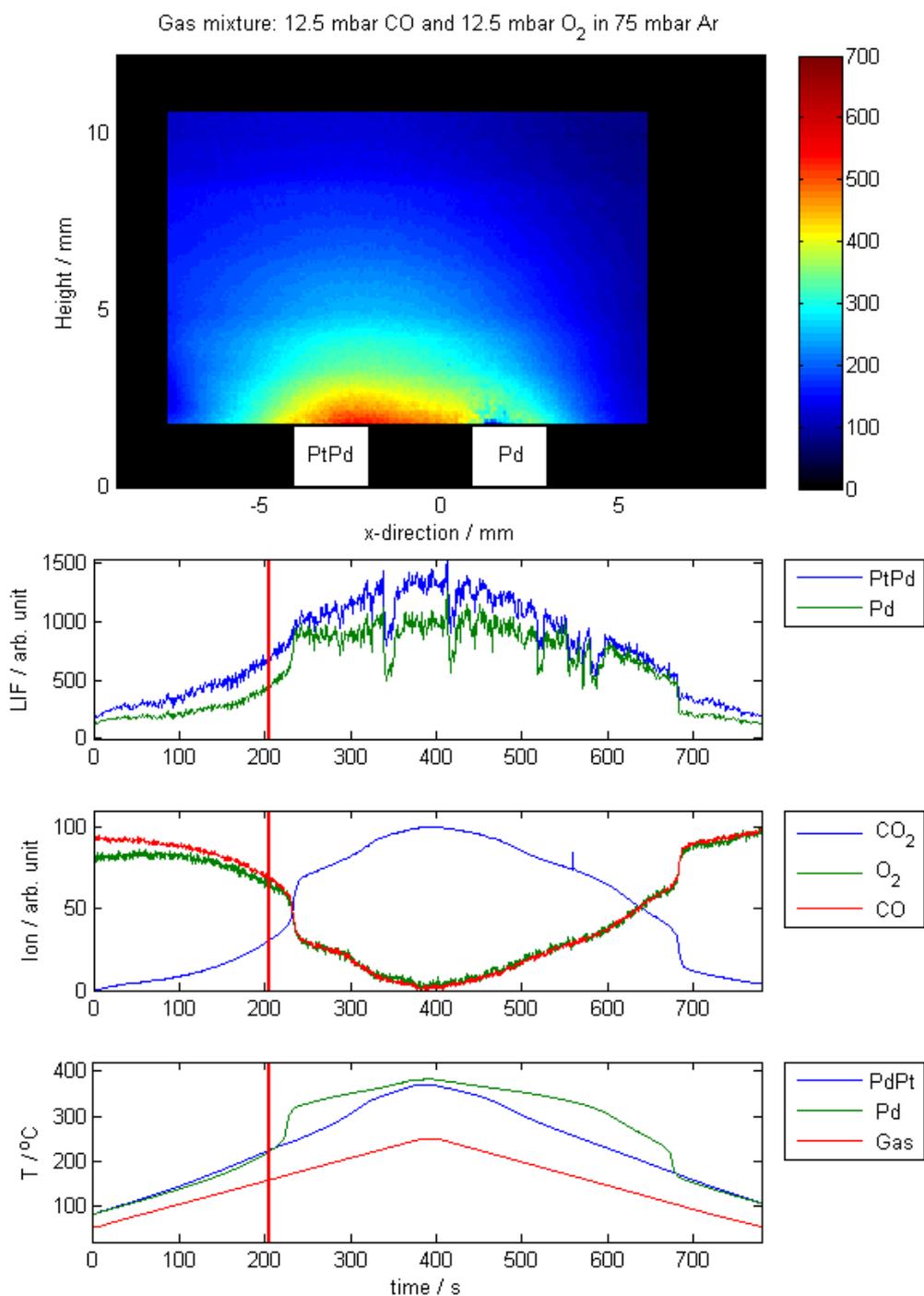


Figure 19. Top image show the LIF signal for a two catalysts measurement, the left sample being 1% Pd, 2% Pt catalyst and the right sample being the 2% Pd catalyst. Below that the LIF signal, mass spectrometer and temperature data were plotted against a common time axis. The red line shows at what time during the measurement the image was taken. The MS data has been normalized and the LIF signal has been compensated for temperature variations.

7. Conclusion

The mass spectrometer shows two parts where CO₂ concentration rapidly increases indicating that a catalyst has become active at both these parts. From that, it is impossible to tell which catalyst became active first and if both catalysts became active or if it was just one of them that became active and then even more active at higher temperature.

The thermocouple shows a temperature on the heating cross while the IR camera shows the same temperature up to a certain point when the temperature suddenly increased for the catalyst indicating that something has happened. At higher temperature similar behavior could be observed for the second catalyst. This means that something has happened to each of them but this measurement cannot see exactly what has happened.

The LIF images show on the other hand that at the same time as the first rapid increase of CO₂ in the mass spectrometer and the increase of temperature for one of the catalysts, the gas surrounding that catalyst was filled with more CO₂ than the rest of the reactor and clear concentration gradients could be observed from the catalyst out to the reactor.

The reactor show great promise for future work. These results indicate that it behaves similar to the reactor presented in ref [10] but with the smaller size a higher spatial resolution can be obtained. This reactor and the rest of the setup also enables for tests with higher flows. And last but not least, the gas inlet and outlet as well as sample holder geometries are the same as for reactors used for surface studies at the ESRF (France), Petra III (Germany) and MAX IV (Sweden), making measurements possible to aid a better understanding for the gas phase conditions at reaction conditions.

8. Outlook

Improvements for the computer program that was created to control the setup could be to get the OPC communication with the MS to work as well as finding a better way to extract data from the IR camera for temperature measurements.

Something this setup is missing is some sort of surface measurement that can be used at atmospheric pressure, e.g. SXR. There are indications that at a certain temperature the surface of catalysts reconstructs and that is when the catalyst becomes active as can be seen in the work by Barroo et al. on rhodium and platinum nanocrystals [13]. If the surface of the catalyst could be examined at the same time as the detectors mentioned above are used, a more complete measurement would be performed and more hints about how catalysts work could be discovered. With this reactor the first steps in this direction have been taken, and can be hopefully simultaneous measurements of SXR and LIF can be achieved in the foreseeable future.

Appendix A – self reflection

During my bachelor thesis I have learned many things concerning practical experimentalist work. Like connecting cables in a smart fashion, making the set up work, finding solutions to all sorts of problems (like one device had a RS-232c cable but our computer only had USB and RS-232 ports) and of course calibration measurements and other more “physics related” things.

Since most of my time during this project was spend getting the computer and the LabVIEW program to work I also learned a great deal about graphical programming and LabVIEW. Alongside this work, I also stumbled across different kind of technical issues similar to the RS-232c problem mentioned previously. I was in contact with two different companies trying to get their hardware to communicate with my computer. At some point we had to order new parts because some parts were broken and other problems like that. There were a lot of independent work where I only had a rough idea what to do since my supervisor told me how he wanted the program to behave (or how the data should look after I processed it) and then I had to figure out how to do that myself. Since neither my supervisor nor I had any experience of LabVIEW most of my time the first couple of weeks were spent figuring out how LabVIEW worked and how I was supposed to send commands from the program to the equipment. During this time I also learned what a PID controller was and how to make one work, even though how well I managed to choose the parameters could be discussed. Although my PID tuning maybe was not the best, it presented me with a new issue, making the temperature ramp work. The important thing was not that it was a perfect PID controller; the important thing was that the temperature was equal to the target temperature. That was something that was useful to learn, results matters, how the results is obtained is of less importance (mostly because we had very little time to do our measurements and the PID problem was something that happened a week before we were supposed to start doing measurements).

When we were close to the measurement weeks, there were planning to do. Although I did not plan how the measurements were supposed to be conducted, communications from my supervisor and the rest of the research group made sure that we all know what would happen when and this was a useful experience to know a way to conduct measurements. When the measurement weeks had passed, the data had to be analyzed and evaluated. Here I learned how to present data in a clear way, the importance of keeping data saved in a structured way so that the file you are looking for can be found and so on. I recorded movies, found important images to show and ran our raw data through all of our compensations. In the data processing part of the thesis, me and their newest Ph.D. student was working together more or less without seeing our supervisor for a week or two.

When the thesis were supposed to be written I had to learn more about the theoretical background of our experiment and the closest related fields, like XPS and SXRD and those techniques. Going through everything at this stage made sure that I had understood what we had been doing more than the general understanding that “we have been looking at a catalyst”.

To summarize; I learned how to make programs in LabVIEW, solving technical issues concerning computer and measurement devices, learned how to process and display data, communicating with my fellow project members, gained a deeper theoretical knowledge of catalysis and LIF, and I now

have a basic idea how it feels working at a university (minus the responsibility that comes with being a “real” employee).

En lysande studie om katalysatorer

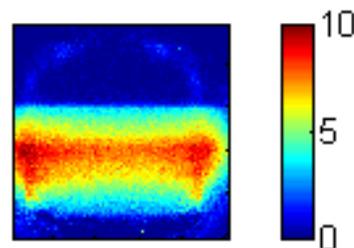
Förbränning är en livsviktig process för vårt moderna samhälle och för att effektivisera processen krävs forskning. Forskningen kan handla om att förbättra bränslesyreblandningen eller omgivningen till reaktionen så att den kan ske effektivare. Den här artikeln handlar om det senare, närmare bestämt katalysatorer och sambandet mellan aktivitet och temperatur.

Det vanligaste användningsområdet för katalysatorer är att reducera farligt utsläpp från bilar genom att underlätta förbränning, eller mer exakt oxidation, av NO_x , SO_x och CO (kolmonoxid). Utan en katalysator i bilen skulle de giftiga gaserna förorena atmosfären och bidra bland annat till surt regn vilket förstör miljön på vår planet. CO som vi primärt har jobbat med är nästan ännu otäckare då den är direkt dödlig att andas in för människor. Det finns även andra sätt att använda katalysatorer på, till exempel inom industrin, vilket minskar mängden energi som behövs användas för att framställa en produkt.

Med hjälp av en laser kan man belysa en gasblandning och genom att studera det utkommande ljuset bestämma vilka ämnen och hur mycket av varje ämne det finns i olika delar av gasblandningen. Lasern används i vår uppställning för att belysa området ovanför en katalysator för att ta reda på hur mycket CO_2 (koldioxid) katalysatorn faktiskt producerar. I en liten kubformad kammare med fönster på sidorna placeras katalysatorn som undersöks. Kammaren fylls med en gasblandning av argon, CO och syrgas (O_2) pumpades förbi katalysatorn så att reaktionen till CO_2 kan ske vid katalysatorn. Argongasen används för att höja totaltrycket i kammaren utan att påverka reaktionen. Katalysatorn värms sedan sakta och skillnader mellan låga och höga temperaturer kunde observeras.

Ett viktigt resultat från studien är att vid en specifik temperatur blir katalysatorn väldigt aktiv; den går från att vara nästan helt inaktiv till att plötsligt producera väldigt mycket CO_2 . Värt att notera är att CO är direkt dödligt för människor eftersom det binder till hemoglobinet i blodet och gör det oanvändbart för syretransport så katalysatorer för den här reaktionen är viktiga att ha.

Slutsatsen som kan dras från allt det här är att det inte bara är viktigt att ha en bra katalysator i bilen utan också ha rätt temperatur på den, annars kör man runt med en (dödlig) miljöbov på fyra hjul. Som tur är ingår värme i de flesta bilmotorer, så börja inte jobba med kall förbränning nu.



Appendix C – In depth programming

The experiment required all of the components to communicate with a computer. There were several reasons for this, one was to be able to take every measured value and match it to a common time stamp. Another reason was that this way everything could be controlled from the computer which is way more convenient then running around the lab having to adjust everything on separate locations.

The things that had to be controlled were: a power supply, a mass spectrometer (MS), a leak valve, three gauges, two thermocouples, a laser beam energy reader, an IR camera and six mass flow controllers (MFC). The program was made in LabVIEW using different ways to communicate with each set of instruments.

The gauges were only supposed to send data to the program which in turn saved it to a file. Using serial ports and Virtual Instrument Software Architecture (VISA), a command was sent from the program to these devices and then they would return a measured value. All VISA IDs were saved in the program as constants so exchanging connection cables to the computer might require change of these constants to make the program work properly.

The thermocouples were connected to a NI device which made it possible to use some of LabVIEW's built-in VIs to receive data from them. A task was created and started outside the while loop of the main program starting a continuous measurement. Then there was a VI within the loop that just read the latest values. Starting and stopping the task every time a value should be obtained (usually four times per second) was not an option as starting the task took around half a second.

The power supply also used a serial port and VISA for communication. It was used for heating and as such it was required that it could be controlled in two different ways. One way was to set a current and then the power supply outputs that current. Another way was to set a temperature and then letting the power supply adjust the current to match the temperature. The latter required the power supply to receive data from one of the thermocouples and then adjusting the current to heat more or less to make the measured temperature become closer to the target temperature using PID control.

The catalytic measurements were conducted by raising the temperature, in one of the two previously mentioned ways, then measuring on the heated sample for some time and finally cooling the sample down to some temperature. If the heating was supposed to be controlled by setting a current, then a linear increase was made by calculating a number (in ampere per second) and that was used to increase the current every update (usually four times per second). Similar when the current was decreased. If the heating on the other hand was controlled by a set temperature the program uses the previously mentioned method trying to adjust the temperature by reading a value from a thermocouple. This was used both for increasing, decreasing and holding the temperature constant. The set temperature increases and decreases linearly similar to the current during increase and decrease phase though. The current was saved to the same file as the temperature and pressures.

The MFCs were also communicating using a serial port and VISA. Although one could control them using Dynamic Data Exchange (DDE) as long as LabVIEW 32-bit was used. When the program was

reset the program reads which gas each MFC was calibrated for and calculates a correction factor if another gas was written to be used in that MFC. The correction factor was then used to calculate new maximum flow capacities through the MFC as well as how much gas actually flows through the MFC. If no gas or the same gas as the MFC was calibrated for the correction factor was one. The program sends a value for flow to the MFCs and they adjust themselves to let enough gas through (if the correction factor is used). A red light was lit in the program if the measured flow differed from the set value with more than $\pm 2\%$. The measured flow values were saved in the same file as all the rest.

The MS could only operate if the pressure was around $4 \cdot 10^{-6}$ mbar so the gas passing the measurement chamber could not be directly led to the MS, but had to go through a leak valve which let some of the gas through. How open the leak valve was could be controlled in a similar fashion to the heating when it was controlled by a set temperature, but instead of a thermocouple it used one of the gauges (the one measuring the pressure near the MS). The leak valve also used a serial port and VISA for communication.

Since the laser beam energy was constantly changing keeping track and logging the energy of the beam was useful. The device communicated through a RS 232c cable. Since the computer only had USB-ports a RS 232c to RS 232 and then a RS 232 to USB was used. The data was collected similar to the thermocouples. A command to start sending data to the computer was sent before the loop within the program. The display on the device showed the same as the values that was sent to the computer. That implied that the display could not display averaged values because then all values would not be logged. When the loop was stopped in the program, the display started to display averaged values again.

Unfortunately, communicating with the MS did not work although there were some VIs with the basis for communication using LabVIEW as an OPC client ready but the filament in the MS would not turn on when receiving commands from LabVIEW. Instead the program QUADERA was used. Since QUADERA and LabVIEW both uses computer time as their time reference, the data would still be synchronized with respect to time.

The IR camera used firewire to communicate with the computer. Using picture acquisition tools within LabVIEW a screen shot from the cameras display was captured. This could then be manipulated to get a temperature within a small region of interest (ROI) which could be marked when the reset button was pressed. The temperature was calculated by using the temperature scale on the image and taking the average pixel value within the ROI and comparing it to the scale. This turned out to not work very well so another computer with a program designed for that camera was used instead during the catalytic measurements.

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