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Kinetic study of oxychlorination process

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1. Background

The ethylene dichloride (EDC) production is rising because of its close connection to the polymer industry as a main reactant for producing vinyl-chloride, the monomer used for the PVC production. There are two common ways to obtain EDC, direct chlorination of ethylene and ethylene oxychlorination. There's not so much information about this second method compared with the first one, that's the main reason why a kinetic study was needed and further knowledge about the catalyst and the process must be reached.

1.1. Vinyl chloride monomer (VCM) obtaining processes

1.1.1. Ethylene direct chlorination

The advantage in this process is that requires lower temperatures and the global process is simpler. Therefore, both operating costs and capital investment are much lower.
The equation 1.1 shows the implied exothermic reaction with an enthalpy of reaction value of -180kJ/mol **[1].**

$$CH_2 = CH_2 + Cl_2 \leftrightarrow ClCH_2CH_2Cl \qquad [1.1]$$

$$FeCl_3 + Cl_2 \leftrightarrow FeCl_3^- - Cl^+ \qquad [1.2]$$
$$CH_2 = CH_2 + FeCl_3^- - Cl^+ \leftrightarrow ClCH_2CH_2Cl + FeCl_3 \qquad [1.3]$$

The catalyst used for this process is ferric chloride because it has a high selectivity (~99%) to EDC and higher conversions (~100%) than the oxychlorination process.

1.1.2. Ethylene oxychlorination

Compared with the direct chlorination process, the oxychlorination doesn't have so many advantages. The main point in the oxychlorination is to consume the HCl generated in the EDC cracking process.
The overall reaction shown in the equation 1.4 is highly exothermic: -239kJ/mol.

$$CH_2 = CH_2 + \frac{1}{2}O_2 + 2HCl \leftrightarrow ClCH_2CH_2Cl + H_2O \qquad [1.4]$$

The catalyst mainly used for this process is cupric chloride. Lanthanum (III) chloride or potassium chloride can also be added in smaller quantities to upgrade the catalyst **[2]**.
A disadvantage of this process is the higher amount of by-products formed and the lower selectivity (94-97% to EDC) of the process compared to the direct chlorination process since higher temperatures are required.

The reaction can be separated in three steps shown in the equations 1.5, 1.6 and 1.7.

$$CH_2 = CH_2 + 2CuCl_2 \leftrightarrow ClCH_2CH_2Cl + 2CuCl \qquad [1.5]$$
$$\frac{1}{2}O_2 + 2CuCl \leftrightarrow CuOCuCl_2 \qquad [1.6]$$
$$2HCl + CuOCuCl_2 \leftrightarrow 2CuCl_2 + H_2O \qquad [1.7]$$

1.1.3. Cracking process

The EDC cracking is the second and last step to get the vinyl-chloride whether the previous step was to obtain the EDC from the ethylene. The overall reaction process is basically an HCl extraction from the EDC molecule.

$$ClCH_2CH_2Cl \leftrightarrow CH_2 = CHCl + HCl \quad [1.8]$$

The mechanism of this reaction is an initialization-propagation-termination process with $Cl^{\cdot}$ as the free radical of the chain process. Operation conditions for this process are quite higher than the EDC formation. Pressures can be set between 1.4 and 3 MPa and the temperature range is 425-550ºC and it strongly depends on the equipment design for each different process and its variables (as mass flow, residence time, equipment size and dimensions, etc).

Unlike the EDC production processes, the EDC cracking is an endothermic reaction with a reaction enthalpy of 71kJ/mol.

Initialization:

$$ClCH_2CH_2Cl \leftrightarrow ClCH_2C^{\cdot}H_2 + Cl^{\cdot} \quad [1.9]$$

Propagation:

$$Cl^{\cdot} + ClCH_2CH_2Cl \leftrightarrow ClCH_2C^{\cdot}HCl + HCl \quad [1.10]$$

$$ClCH_2C^{\cdot}HCl \leftrightarrow CH_2 = CHCl + Cl^{\cdot} \quad [1.11]$$

Termination:

$$Cl^{\cdot} + ClCH_2C^{\cdot}H_2 \leftrightarrow CH_2 = CHCl + HCl \quad [1.12]$$

In this process there’s a big amount of HCl produced. This is why the oxychlorination process takes more importance against the direct chlorination; the HCl needs to be re-used to avoid it from accumulation.

1.2. Methodology

The procedure during the experiments changes depending on the stage of the research.
First of all the kinetic information of all three single steps is needed. Therefore the experiments are run in such a way where one reaction step is run at a time. This way the reactions [1.5], [1.6] and [1.7] can be studied separately and a kinetic model can be proposed for every step.
In the figure 1.1 the cycle composed by the three reaction steps is shown with the three different catalyst states on the triangle’s vertices.

Once this part is completed some experiments with more than one step running at a time can be performed. With the parameters fitted from the single step experiments, the model can be checked by comparing the predicted results with the obtained results from these experiments. Finally some experiments with all three reactants can be performed so the results can be compared again against the proposed model.

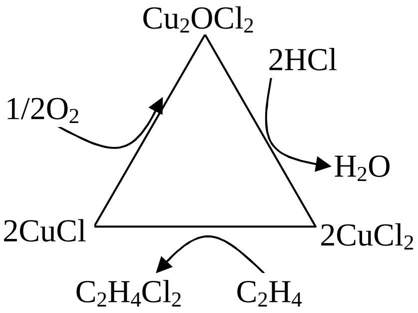


Figure 1.1 Cycle of the three reaction steps.

Depending on what is studied, the operating conditions might change. For the kinetic study many experiments at different partial pressures and temperatures are needed. The range of temperatures goes from 210ºC to 250ºC; higher temperatures have not been used because considerable deactivation was seen at 250ºC after few 3-reaction-steps cycles. The partial pressure change depending on the compound we focus on, the complete information about the experiments done can be seen in the table 3.1.

In various experiments the reproducibility of the catalyst was studied. Therefore the conditions were set constant all along the set of experiments.
Another condition being changed in some cases is the time in order to find the reaction step where the catalyst was deactivating the most.

2. Experimental

2.1. Measurements

Two main devices were used during all the experiments in order to get the necessary data from the reactions: a Mass-Spectrometer (MS) and Ultraviolet visible emissor/detector (UV-vis). With the MS the amount of every one of the compounds in the reactor outlet stream can be known. The UV-vis provides the information about the catalyst surface state and a connection between the reaction evolution and the UV-vis spectra it’s also expected (see section 3.7.).

After checking that HCl was adsorbing in the MS (see 3.5.), probably in the capillary lines, the MS usage was discarded for the third step (eq. **[1.7]**) because of the poor trustworthy data obtained. On its place a pH-meter started to be used by measuring the acidity of a known amount of distilled water where the reactor outlet stream was being bubbled.

2.1.1. UV/Vis spectrophotometer

2.1.1.1. Ultraviolet spectroscopy technique

The UV/Vis spectroscopy is commonly used to identify functional groups in studied compounds by locating the bands in an UV/Vis spectrum.
This technique is based on the principle that, when a molecule absorbs the UV-radiation, an electron is promoted to an excited state. In each situation electrons need different wavelength to become excited. Therefore, with a wide database with information about which wavelengths excites every bond/orbital, the bands in a UV spectrum can be compared to identify the nature of the analyte.

As seen in the picture 2.1 the spectrometer used is an AvaSpec-3648-USB2 And the light bulb used is the Halogen one from the AvaLight-DHS connected to the emissor that is pointing the catalytic bed in the reactor.

The software used is the AvaSoft for AvaSpec-USB2 version 7.5.

Figure 2.1 Ultraviolet-visible spectrophotometer device used in the experiments.

2.1.1.2. UV-vis data

Before starting the experiments, a blank must be done. For all the experiments the compound used for the blank is $BaSO_4$, so all the UV-vis data is referred to that.
When the blank is done and the catalyst is load ready to start the experiments, the recording of the Reflectance vs. Wavelength can start. For almost all the experiments done the spectra was saved every 30 seconds, the time lapse is good enough for the first two steps and no big gaps are found there. For the third step it was found lately that the spectra showed changes in a short period of time so for this step the spectra should be save every 5 seconds.
In the latest experiments the spectra was saved every 5 seconds in all three steps to ensure that all the important data is being recorded.

From the data obtained in the experiments the method explained in the section 2.3.3. is followed. The absorption edge energy (AEE) and the maximum peak value in the Kubelka-Munk Function can be used to set a relation with the reaction such as the outlet EDC amount for the first step or the reacted O2 amount for the second one at any time (see section 3.7.).

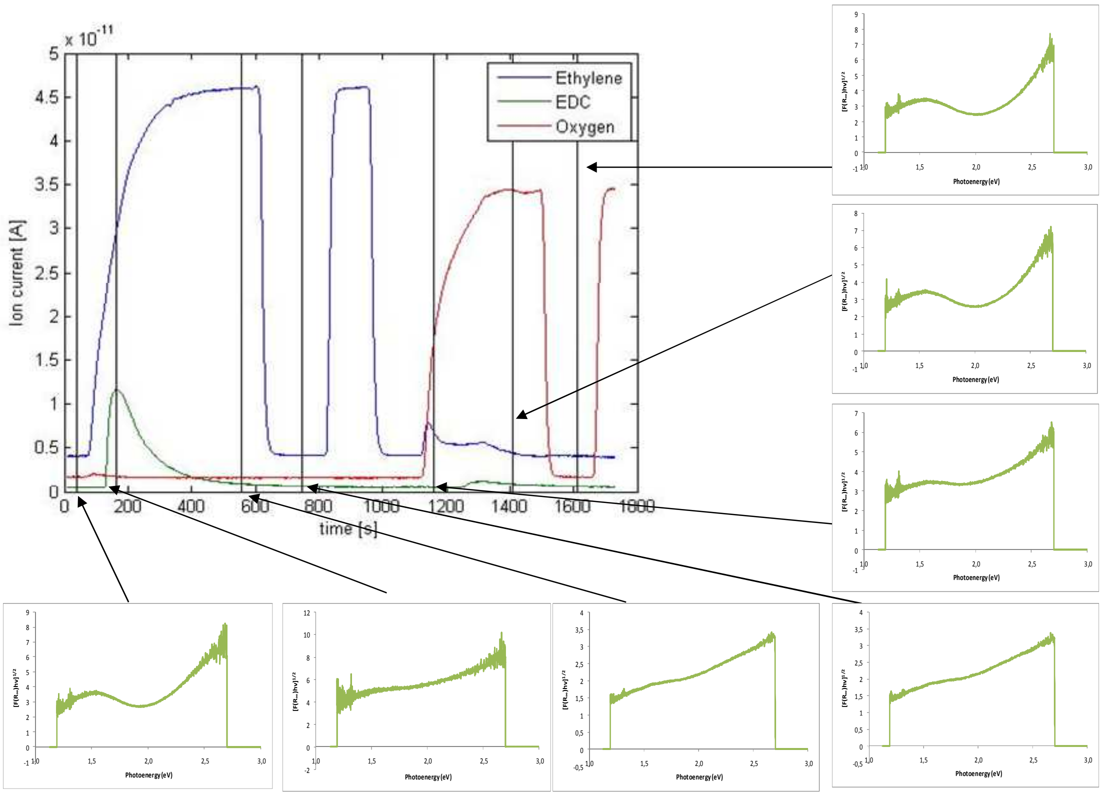


Figure 2.2 Example of UV-vis spectra.

In the figure 2.2 a example of UV-vis spectra shows the shape and changes of the spectra during the first two steps of the experiments where the main changes in the catalyst are done. In the first step the copper is reduced from Cu^{2+} to Cu^{+} and during the second step is oxidized again.

2.1.2. MS

2.1.2.1. Mass spectrometry technique

The mass spectrometry is a technique really useful since it can measure quantitatively the composition of a sample with a high precision. In fact, the MS measures the ionized molecules from the mentioned sample so there could be more than one signal corresponding to the same compound with different ionization level.

In this study the MS provides the spectrum from which the kinetic transient profiles can be obtained and used to fit some kinetic models later on.
A MS has three main parts that are described in the next lines. Besides that, there will be also the physical principles from which the design of the MS parts was based.

- **Ionization source**: The first part of the MS, here the analyte is ionized. There's a filament which provides the electrons and a trap electrode which receives the flux of electrons and stabilizes the emission. Through this electron flux the analyte (in this case a continuous stream) goes on and after the collision with the electrons, the molecules in the stream are ionized, ready to the next step in the MS.

- **Mass analyzer**: Since the stream is ionized a separation method has to be applied to distinguish the different compounds. The MS uses the mass differences to separate the different molecules of the stream. The way to do it is by applying a magnetic field or an electrical field; this would generate a force to all the ionized molecules. The point on this is that the molecules have the same lineal velocity and the same strength applied, therefore the acceleration applied on each molecule depends on the mass; the highest-mass molecules will trace a curve with wider radius and the lowest-mass ones will trace a curve with shorter radius.
  Then, the higher the molecule mass is the farther is found from the curve's center of curvature. In the figure 2.3 a scheme of the previously explained is shown. So far was supposed that the charge from the ionization was constant among all the molecules, but that's not true. A molecule can be more charged than another one and the charge acts inversely proportional to the mass: The higher the charge is the shorter is the radius of the curve traced.
  This design of the MS is based on the Lorentz force law [2.1] that relates the electric or magnetic field with the particle velocity, charge and strength applied.

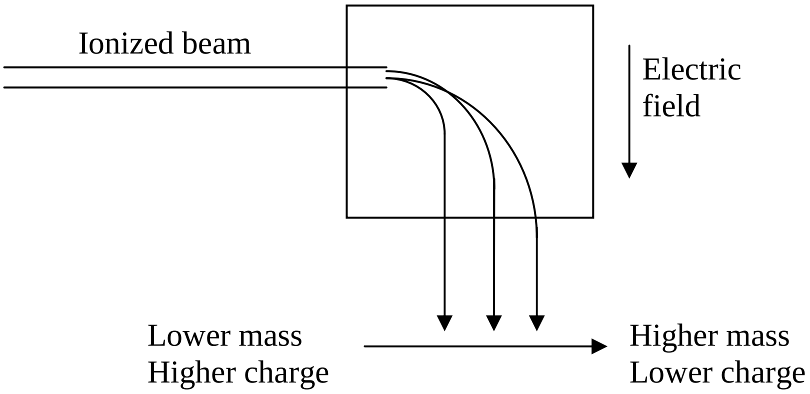


Figure 2.3 Example of how the MS separates the molecules of different size and charge.

- **Detector**: Finally, there's the part where the ionized molecules collide with the detector. Since the particles are separated depending on their mass-charge ratio, the intensity detected of each type of ion is easy.

Lorentz's force law:

$$\vec{F} = q \cdot (\vec{E} + \vec{v} \times \vec{B}) \quad [2.1]$$

Newton's law:

$$\vec{F} = m \cdot \vec{a} \quad [2.2]$$

Combining the equations [2.1] and [2.2]

$$\frac{m}{q} = \frac{(\vec{E} + \vec{v} \times \vec{B})}{\vec{a}} \quad [2.3]$$

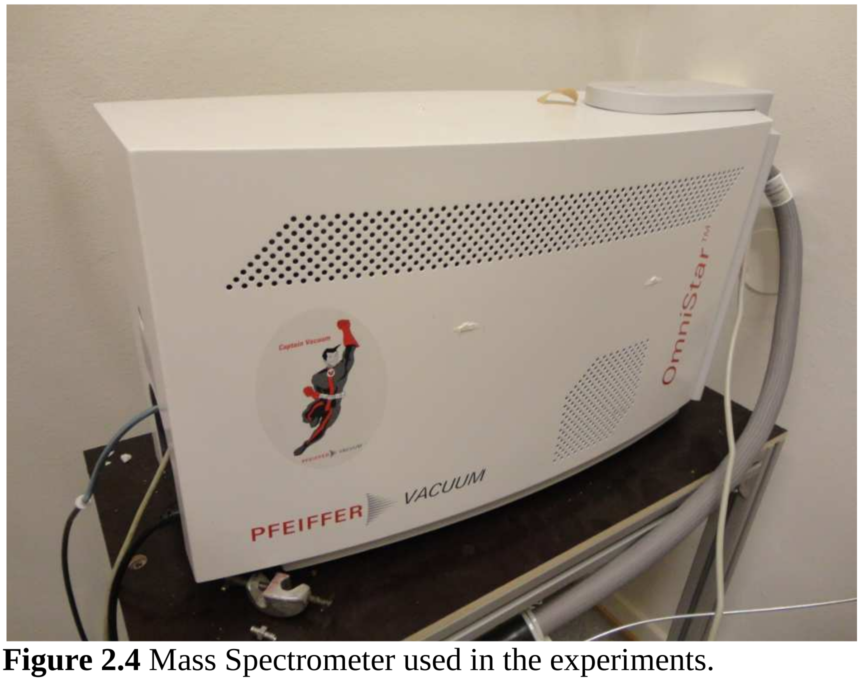


Figure 2.4 Mass Spectrometer used in the experiments.

2.1.2.2. MS data

The analyzed stream is the reactor outlet flow so the reaction products, unreacted compounds and the inert gases can be detected. Once the compounds reach the MS detector, the ion amount is measured and it's displayed on the MS screen plot.
On these profiles, the Intensity vs. time plots can be seen for each ion, there's a little delay time before the MS registers any change made in the process (like opening/closing valves or changing flows) but this is not a problem since the important part in the profiles is their shape and their development versus the time.

The blank from which a comparison with the experimental data can be done is recorded right after the end of the reaction when the reactant is not supposed to react with the catalyst anymore. Unfortunately in some early experiments an overshoot was observed during only the reaction part, not in the blank part. This phenomenon could be explained by a punctual heating up in the catalytic bed due to the exothermic reaction which might cause an acceleration of the flow because of its expansion effect under the effect of a temperature increase.
Under these circumstances a second blank system recording was performed. An inert gas was injected in the reactor at the same time with the corresponding reactant for each step. The inert gases used were either Ar or He and the gas ratio between the inert gas and the reactant was previously known. Therefore, the MS could record both reactant and inert amounts and since the gases ratio was known, the theoretical reactant amount could be predicted from the inert gas profile.

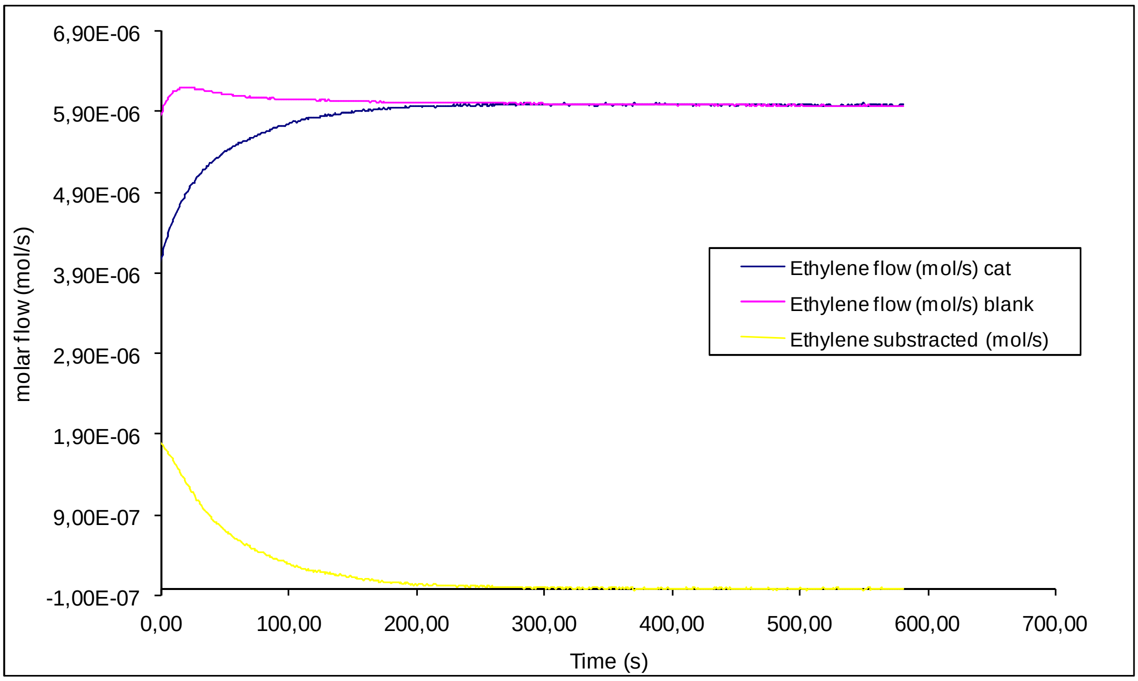


Figure 2.5 Blank line calculated from the Ar data, ethylene profile during the experiment and EDC amount calculated.

2.1.3. pH-meter

2.1.3.1. pH recording technique

During the step in which the chlorination reaction was studied, for some late experiments, the pH-meter was used in order to measure the pH from a solution where the reactor outlet stream was being bubbled. Therefore the amount of HCl not reacted would be absorbed and measured by the pH-meter.

The reason why this method is used for the third step instead of the MS is because HCl adsorption was detected on the MS capillary tubes and the data obtained from those experiments are not good to use.
Obviously the pH-meter has a precision much lower than the MS and that's the drawback of this method. Since the HCl flow is constant, the concentration of HCl absorbed rises linearly and that makes a logarithmical profile for the pH which cause a lot of error after some minutes when the pH reaches low values and its decreasing rate gets slower and slower. Fortunately this step is quite fast and it is normally finished after reaching the high error area.

2.1.3.2. pH data

For this experiment distilled water was used as absorbent for the HCl. The amount of water was calculated in a way that the concentration doesn't rise too fast and the pH curve at the beginning of the experiment has a smoother profile.
Finally the volume of water used is 2 liters, higher volumes would provide better profile definition at the beginning of the experiment and lower volume would be useful to run the experiment for longer time with less error. The decision came from a compromise between these two statements.

A blank for these experiments is needed too. As explained in 3.5. there's HCl adsorption on the catalyst support. Therefore this has to be taken into account when calculation the HCl consumed by the reaction.
For the blank experiment the reactor is loaded with the corresponding weight of support γ-Al_2O_3 that was used in the experiments as a part of the catalyst. This way the mass of support in both experiment and blank would be the same. The temperature is set to the experiment temperature and then the HCl amount in the reactor outlet stream is recorded with the pH-meter.
By using this system it is supposed that the catalyst presence in the support won't affect the amount of HCl adsorbed per gram of support which it's not clear if it's true.

2.2. Catalyst

The catalyst used for the chlorination of the ethylene is $CuCl_2/\gamma$-Al_2O_3. In this case, when the first reaction is in process the chlorine reactant is directly removed from the surface of the catalyst.

When chlorinating the catalyst, the amount of Cl^- loaded to the catalyst remains theoretically constant and that depends on the amount of Cu^{2+} loaded at first during the preparation of the catalyst. Therefore, after the preparation of the catalyst, there's a maximum amount of chlorine that can be loaded on the catalyst. Some more chlorine is seen to be adsorbing on the support in addition of the catalyst as explained in the section 3.5.

2.2.1. Active compound

In order to spread it all around the support surface the wetness impregnation method is followed. In the section 2.3.1 further explanations about the procedure can be found.

Even though both Cu^{2+} and Cl^- were loaded on the support, the Cl^- is not really a part of the catalyst. The active site is the copper so this and the support are the two different parts composing the catalyst. The Cl^- is just adsorbed on the surface ready to react with ethylene as one of the reactants for the production of EDC.

2.2.2. Preparation of the Catalyst

When a catalyst is going to be prepared, the main parameter that has to be set is the copper load which is recommendable to be within the range of 1%-6%. Higher copper loading might cause the layer of copper to aggregate in bigger particles on the support surface.

Once the support mass is weighted the theoretically mass of $CuCl_2$ can be calculated as described in 2.3.1. When weighting the mass of $CuCl_2$ there's no need to get the exact calculated mass because the copper load is calculated afterwards from the weighted compound amounts.

After the mass of $CuCl_2$ is known, the mass of water needed is calculated so the water uptake of the support equals the water in the $CuCl_2 \cdot 2H_2O$ + H_2O mixture prepared, known as incipient wetness impregnation method.
After the impregnation, the catalyst is dried in an oven at 120ºC overnight.

Finally the catalyst can be sieved using the sieves so the final catalyst can be obtained with a diameter between 75 and 150μm. When the amount of catalyst obtained from the sieving is not that much, a pellet machine is used in order to get bigger particle diameters.

2.3. Calculations and data processing

All the calculations implied in the data treatment are further explained in the following.

2.3.1. Catalyst preparation

During the preparation of the catalyst, some calculations need to be done in order to know the amount of $CuCl_2$ and H_2O that is going to be used to prepare the impregnating solution.

First of all a copper load has to be supposed. The definition of this load is the fraction of copper mass in the catalyst after its preparation. In the equation [2.4] this definition is expressed in equation form:

$$w_{Cu} = \frac{m_{Cu}}{m_{sup} + m_{CuCl_2}} \qquad [2.4]$$

Due to the fact that only $CuCl_2$ dihydrated is available, the equation 2.5 is needed to replace the unknown variables as m_{Cu} and m_{CuCl2}.

$$m_i = \frac{M_i}{M_{m_{CuCl_2 \cdot 2H_2O}}} \cdot m_{CuCl_2 \cdot 2H_2O} \qquad [2.5]$$

i: index valid for Cu and $CuCl_2$

In the equation [2.5] there's the molar ratio between $CuCl_2 \cdot 2H_2O$ and both Cu / $CuCl_2$ missing. This is so because it's obvious that this ratio must be equal to 1, therefore the stoichiometric coefficients have not been written in this formula.

Combining equations [2.4] and [2.5] and isolating the dihyrated $CuCl_2$ mass, this can be calculated from the mass amount of support and the copper load wanted for this catalyst:

$$m_{CuCl_2 \cdot 2H_2O,t} = \frac{w_{Cu} \cdot m_{sup} \cdot M_{CuCl_2 \cdot 2H_2O}}{M_{Cu} - w_{Cu} \cdot M_{CuCl_2}} \qquad [2.6]$$

Evaluating the equation [2.6] there's a consideration that needs to be taken into account. The denominator part of the equation shown $M_{Cu} - w_{Cu} \cdot M_{CuCl2}$, this term can reach a value of 0 when $w_{Cu} = M_{Cu}/M_{CuCl2} \approx 0.473$ and this means the mass of dihydrated $CuCl_2$ tends to infinity for such copper load. This happens because besides the copper load when preparing the catalyst, there's also a load of Cl that is taken into account when calculating the w_{Cu}.

Anyway this shouldn't be a problem because low mass fractions of Cu are being used.

The next step focuses on knowing the amount of water where the $CuCl_2$ has to be dissolved. The incipient wetness impregnation method is followed in order to know the exact mass of water that the support can uptake. For this calculation the water molecules hydrated in the $CuCl_2$ salt was taken into account.

As can be seen in the equation [2.7] the subtraction term on the right part corresponds to the amount of water that is actually in the $CuCl_2$ salt.

$$m_{H_2O,t} = PV \cdot m_{sup,r} - H_{CuCl_2} \cdot m_{CuCl_2 \cdot 2H_2O,r} \cdot \frac{M_{H_2O}}{M_{CuCl_2 \cdot 2H_2O}} \qquad [2.7]$$

Both water and $CuCl_2$ calculated masses are the exact theoretically amount of each one. During the catalyst preparation there's no need to get the exact calculated number but a close one. Therefore, as the final calculation step the real copper load can be found.

The equation [2.9] shows the way to calculate the copper load. The root of this equation is the equation [2.4] but with one added parameter. Since it is possible that the impregnating solution had not been completely used, the following mass fraction is introduced in the formula:

$$w_{impregnated} = \frac{m_{impregnated}}{m_{CuCl_2 \cdot 2H_2O,r} + m_{H_2O,r}} \qquad [2.8]$$

Which simplifies the final equation to:

$$w_{Cu} = \frac{M_{Cu}}{\dfrac{m_{sup,r} \cdot M_{CuCl_2 \cdot 2H_2O}}{w_{impregnated} \cdot m_{CuCl_2 \cdot 2H_2O,r}} + M_{CuCl_2}} \qquad [2.9]$$

When it comes to introduce dopant compounds the calculation change a little bit. Not only has the copper load to be set but also the molar ratio between copper-potassium-lanthanum. In the formulas the variable “*ratio*” corresponds to the number of moles of the specified compound (e.g. If the Cu-K-La is 5-1-1, the “*ratio*” values for Cu, K and La would be 5, 1 and 1 respectively).

In the equation [2.10] there’s the definition for the W_{Cu} in this case, which is an extension of the equation [2.4].

$$W_{Cu} = \frac{m_{Cu}}{m_{sup} + m_{CuCl_2} + m_{KCl} + m_{LaCl_3}} \qquad [2.10]$$

For the masses of KCl and LaCl3 to be substituted, the equation [2.11] can be used.

$$m_i = \frac{M_i}{M_{m_{CuCl_2 \cdot 2H_2O}}} \cdot m_{CuCl_2 \cdot 2H_2O,t} \cdot \frac{ratio_i}{ratio_{CuCl_2}} \qquad [2.11]$$

i: index valid for $CuCl_2$, KCl and $LaCl_3$

Now the amount of CuCl dihydrated can be known from the equations [2.10] and [2.11].

$$m_{CuCl_2 \cdot 2H_2O,t} = \frac{w_{Cu} \cdot m_{sup,r} \cdot M_{CuCl_2 \cdot 2H_2O}}{M_{Cu} - w_{Cu} \cdot \left(M_{CuCl_2} + M_{KCl} \cdot \dfrac{ratio_{KCl}}{ratio_{CuCl_2}} + M_{LaCl_3} \cdot \dfrac{ratio_{LaCl_3}}{ratio_{CuCl_2}} \right)} \qquad [2.12]$$

Since the ratio of Cu-K-La was set before, the KCl and $LaCl_3$ masses can be known by using the equation [2.11]. At this point, the only variable remaining to be calculated is the water mass for the solution preparation and the further impregnation. The equation [2.13] shows that the amount of water to be weighted is the amount that the support can uptake minus the water already present as hydrated water n the $CuCl_2$ and $LaCl_3$ salts.

$$\begin{aligned} m_{H_2O,t} &= PV \cdot m_{sup,r} \\ &- H_{CuCl_2} \cdot m_{CuCl_2 \cdot 2H_2O,r} \cdot \frac{M_{H_2O}}{M_{CuCl_2 \cdot 2H_2O}} - H_{LaCl_3} \cdot m_{LaCl_3 \cdot 7H_2O,r} \cdot \frac{M_{H_2O}}{M_{LaCl_3 \cdot 7H_2O}} \end{aligned} \qquad [2.13]$$

Once all the compounds are weighted the real copper load can be calculated

$$w_{Cu} = \frac{M_{Cu}}{\dfrac{m_{sup} \cdot M_{CuCl_2 \cdot 2H_2O}}{w_{impregnated} \cdot m_{CuCl_2 \cdot 2H_2O,r}} + \left(M_{CuCl_2} + M_{KCl} \cdot \dfrac{ratio_{KCl}}{ratio_{CuCl_2}} + M_{LaCl_3} \cdot \dfrac{ratio_{LaCl_3}}{ratio_{CuCl_2}} \right)} \qquad [2.14]$$

2.3.2. MS data processing

The MS records the intensity of each ion, that's why a method is needed to convert these data into molar flow. From the calibrations of the MFC shown in 2.3.5 the volumetric flow can be calculated, using the ideal gas equation the molar flow can be known. The way to correlate the intensity signal and the molar flow is by measuring the intensity increase when the known flow is injected and that difference in the intensity signal will be the equivalent of such molar flow. Then the flow during the kinetic stage can be known by applying a simple proportionality. The equation [2.15] shows how it's calculated.

The numerical method is applied in the range of values i = [1, 2, 3 ... N-2, N-1, N]. Where N is the total number of points recorded.

$$\dot{n}_i = \frac{I_i - I_{min}}{I_{max} - I_{min}} \cdot \dot{n}_{max} \qquad [2.15]$$

Since the molar flow of the products, like EDC, is not known, the equation [2.15] cannot be used. There are two different methods for knowing the product molar flow using a blank system.

The first one was used in the early experiments and it consisted of re-injecting the reactants after the reaction, no reactants would be consumed and the shape of the Intensity vs. Time curve could be compared with the one where there was reaction. The difference in the intensity when both curves were overlapped would show the consumed reactant (see equation [2.17]). Unfortunately some problems appeared using this method. An overshoot in the flow showed up during the reaction (both reactant and inert had it) and not during the blank as explained in the section 2.1.2.2. There were some cases where the overshoot was not intense but some other times it would rise even higher than the blank curve; this would make the data unusable.

For this reason a second blank method was proposed and used. In this case the blank curve wouldn't come from a secondary record with fully reacted catalyst. It would be taken from the inert gas (Helium or Argon) that is used for lowering the partial pressure of the reactants. Since the molar ratio between the reactant and the inert flow is known, the theoretical amount of reactant could be calculated from the amount of inert gas and that ratio. This ratio is normally calculated at the end of the experiment, when the reaction is over and both inert and reactant flows reach their steady state.

Then, if there were an overshoot, it would affect both inert and reactant so this problem would be solved because the overshoot in the inert gas flow would be used to correct the theoretical reactant flow.

$$\dot{n}_{blank,i} = \dot{n}_{inert,i} \cdot \frac{\dot{n}_{reactant,ss}}{\dot{n}_{inert,ss}} \qquad [2.16]$$

$$\dot{n}_{product,i} = \dot{n}_{blank,i} - \dot{n}_{reactant,i} \qquad [2.17]$$

Once the product flow is known, the reaction rate can be calculated. In the equation [2.19] the reaction rate is calculated depending on the catalyst mass but it could also be calculated depending on the copper mass by including the copper load in the equation.

$$X_i = \frac{\dot{n}_{product,i}}{\dot{n}_{blank,i}} \qquad [2.18]$$

$$r_{product,i} = \frac{X_i \cdot \dot{n}_{blank,i}}{m_{cat}} \qquad [2.19]$$

The amount of Cl^- of CuCl reacted can be known directly from the reacted reactant. In the equation [2.20] the integral uptake of any of these compounds is calculated. This information will be useful afterwards when plotting the reaction rate versus the remaining compound (Cl^- for the first step and CuCl for the second one).

$$IU_i = \frac{\dot{n}_{product,i} \cdot \Delta t}{m_{cat} \cdot w_{Cu}} + IU_{i-1} \qquad [2.20]$$

For the first step, the theoretical total amount of chlorine loaded can be calculated in mol using the equation [2.21] which relates the total mass of the sample and the w_{Cu}. This chlorine is the total chlorine that would be in the catalyst in the hypothetical case that every one of the copper atoms had two chlorine atoms bonded.
With this value and the calculated integral uptake of chlorine from the experiments, the % of reacted chlorine can be calculated with a simple division.

$$Chlorine\ amount = \frac{m_{cat} \cdot w_{Cu}}{M_{Cu}} \cdot \left[\frac{2\ mol_{Cl}}{mol_{Cu}}\right] \qquad [2.21]$$

The same equation [2.21] can be used to calculate the available CuCl only changing the ratio of 2 mol_{Cl}/mol_{Cu} for 1 mol_{CuCl}/mol_{Cu}.

2.3.3. UV-vis data processing

The data processing for the UV-vis spectra is quite simpler. The raw data obtained shows the % reflectance for each wavelength (nm). Using the equation [2.22] the photon energy is calculated from the wavelength in nm, the Planck constant in eV·s/cycle and the speed of light in m/s.

$$h\nu = \frac{h \cdot c \cdot 10^9}{\lambda} \qquad [2.22]$$

The Kubelka-Munk function [2.23] is used as a previous step in order to get the adsorption edge energy (AEE) from the UV-vis spectra and the maximum value of the peak from which a correlation with the MS data is done in the section 3.7.

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty} \qquad [2.23]$$

$$[F(R_\infty) \cdot h\nu]^{1/2} \qquad [2.24]$$

Then the [2.24] is plotted versus the photon energy. In order to obtain the AEE a linear fitting in the slope of the peak has to be done. The photon energy value where this line intercepts with the minimum energy value of the peak is the AEE.

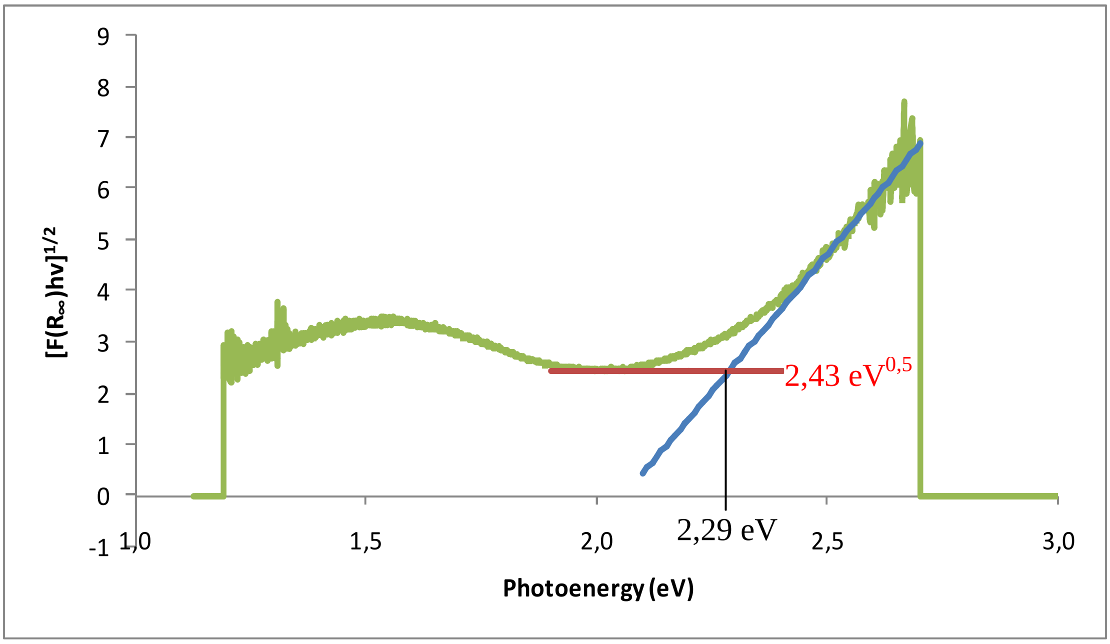


Figure 2.6 Example of how the AEE is obtained.

The blue line in the figure 2.6 is the linear fitting for the slope on the side of the peak. The red line is the minimum energy in the KMF (2,43 $eV^{0,5}$) and there is where the blue line is wanted to be intercepted. In this example the AEE is 2,29 eV because it's the photon energy value of that interception point.

2.3.4. pH-meter data processing

The pH-meter gives no big trouble for the data processing. The equation [2.25] shows the direct relation between the pH and the molar concentration of HCl.

$$[HCl]_i = 10^{-pH_i} \left[\frac{mol}{l}\right] \qquad [2.25]$$

Two different blanks were recorded in order to get more information from this step. One blank was recorded with the reactor empty because some little amount of HCl was adsorbing on the lines. Therefore this could correct the data erasing the HCl-to-line adsorption from the experimental data.

Another blank was needed because it was discovered that the HCl was highly adsorbed by the support used in the catalyst: γ-Al_2O_3. Then the blank was recorded using the corresponding mass of support that was present in the catalyst during the experiment. The reactor would be filled with only that support and then the amount of HCl adsorbed on the support and the lines could be withdrawn from the experimental data. See section 3.5. for further information about this.

2.3.5. MFC calibration

A calibration for the MFC was done so the flow of each compound can be known from the % of the maximum flow available in the MFC. For some compounds the same MFC is used and a selector valve is disposed just before to choose which compound is going to be used. The following equations show these calibrations.

$$\dot{V}_{Ar\,pure} = 0.03926 \cdot Ap_{Ar\,pure} \tag{2.26}$$
$$\dot{V}_{He\,pure} = 0.0393 \cdot Ap_{He\,pure} \tag{2.27}$$
$$\dot{V}_{Ar} = 0.02703 \cdot Ap_{Ar} \tag{2.28}$$
$$\dot{V}_{He} = 0.0275 \cdot Ap_{He} \tag{2.29}$$
$$\dot{V}_{C_2H_4} = 0.1512 \cdot Ap_{C_2H_4} \tag{2.30}$$
$$\dot{V}_{Air} = 0.1229 \cdot Ap_{Air} \tag{2.31}$$
$$\dot{V}_{O_2} = 0.1166 \cdot Ap_{O_2} \tag{2.32}$$
$$\dot{V}_{HCl} = 0.01362 \cdot Ap_{HCl} \tag{2.33}$$

2.4. The setup

The experiments were performed in a setup whose configuration is explained next.
In the figure 2.7 the setup process flow diagram is displayed with a properly explanation of the instruments and equipments used for its correct operation and control.

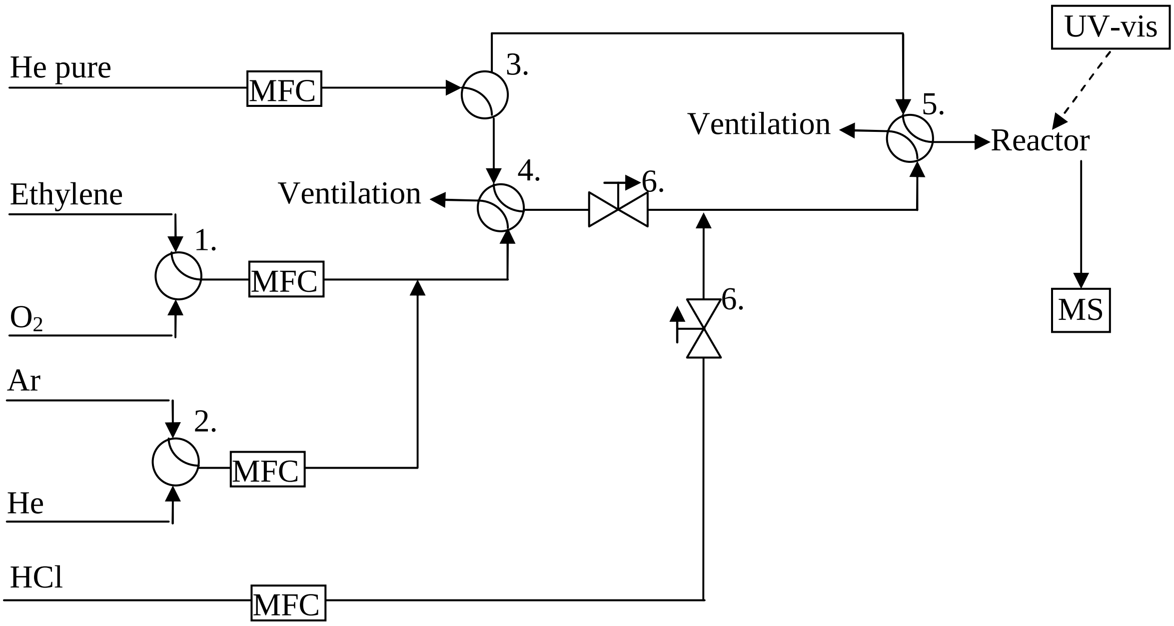


Figure 2.7 The PFD of the setup used for the experiments.

Notes for the figure above:

1. 3-way-valve used to let either ethylene or oxygen through the setup.
2. 3-way-valve used to let either argon or helium through the setup.
3. 3-way-valve used to select in which 4-way-valve the argon must flow.
4. Remote controlled 4-way-valve used to change the argon flow to the ethylene/air flow in a short period of time when starting the experiment.

5. Manual 4-way-valve used to change the argon flow to the hydrochloric acid flow when starting the experiment.
6. Check valves used to avoid backflow.

The reason of having two inert gas streams is that one (Helium pure) is used to flow as an inert through the reactor while the stream of the next experiment is being prepared. The other stream (Argon/Helium) is used to mix with the ethylene or the air in order to set low dilutions of reactants.

2.5. Experiments operation

The procedure followed in each different part of the experiment is explained below.

2.5.1. Catalyst activation

Once the reactor is loaded with the catalyst, placed and attached to the setup the catalyst has to be activated. Two different activation methods have been used and compared in different experiments (see section 3.3.).
The first method followed consists on setting a temperature of 220ºC in the reactor with only inert gas flowing during 50 minutes. During this time most of the moisture will be removed and the catalyst will be partially activated. After this, the ethylene chlorination step would be run but it was observed that during the first cycle of experiments the catalyst was not fully activated. For that reason a second activation method was proposed.

Instead of beginning with the ethylene chlorination after 50 minutes at 220ºC, the oxidation is run. It was thought that a longer time during the second step would oxidize all the Cu^{+} to Cu^{2+} and the catalyst would be ready and fully activated from the second cycle of experiments on.

2.5.2. Ethylene chlorination

During this step the compounds used are He pure, He and ethylene. Through one line in the remote controlled 4-way-valve there's only He pure flowing and through the other there will be both ethylene and He. Since the ethylene used is already a mixture of 5% C_2H_4 in Ar, the Argon from that mixture will be used for the blank in the MS so there's no need of knowing the ratio C_2H_4/He.

Before starting the experiment only He pure will be flowing through the reactor, but after some minutes, when it is made sure that all flows are in steady state, the experiment can start by switching the remote controlled 4-way-valve and changing the He pure flow for the C_2H_4/Ar + He.

2.5.3. Oxidation

It is important to make sure which compound is being used here. In most of the experiments done a gas bottle of pure O_2 was used, but also air can be used for this step, in this case the N_2 can be used as the inert gas for the blank calculation since the ratio N_2/O_2 is already known as 79/21.

So in case that pure oxygen is used, it is important to select Argon as the inert gas which is mixed with the oxygen. The reason for doing this is that in the inert stream there is helium flowing (He pure) and in case the He is selected to be mixed with the oxygen, there would be an overlapping with the He pure and there would be no way to calculate a blank curve for the oxygen.

The way to start the experiment is the same as n the previous step, when all flows reach the steady state the remote controlled 4-way-valve can be switched.

2.5.4. Catalyst chlorination

For this third step HCl, He and He pure are used. Since HCl is troublesome to be measured with the MS, it will be measured by using a pH-meter. Therefore there’s no need to use the inert gas flow or the blank.

When the experiment has to be started the manual 4-way-valve is the one that has to be used. It only has to be ensured that the 3-way-valve in the He pure line is redirecting the flow to the manual 4-way-valve.

3. Results

3.1. Experiments done

A method for naming the experiments was strictly followed. Each set of experiments have between 5 and 8 experiments and normally a set of experiments is run during a single day. Each one of these experiments might have from 1 to 3 steps; normally in the first and last experiment of a set not all the steps are run because it depends on which step is chosen to begin/finish the set of experiments.

The experiments done, listed below in the table 3.1, were planned in such a way that the parameters for different kinetic models could be fitted and, therefore, a discussion of which model is predicting the reaction the best can be done.
Some experiments were focused on the reproducibility of the catalyst. The activity of the catalyst can be compared during the different cycles in a set of experiments. Moreover different temperatures were used in different sets of experiments in order to see how this is affecting the deactivation of the catalyst; also different experiments were planned where the time of one of the steps was much longer than usual. This was done for two out of the three steps in order to know which the step was where the deactivation was more significant.

There are some other experiments where the main point of study is not the reaction or the catalyst but the study of one of the compounds, in this case HCl. Those kinds of experiments were run with the empty reactor, only support or with a change in the setup piping so the problems related with the HCl adsorption could be identified.

All the experiments done had a total pressure operation of 1 atmosphere. It was risky to operate at higher pressures because the setup might not be prepared for that conditions and some leakages could appear if there were any kind of damage in any of the setup lines or fittings. For this reason and because of the lack of necessity for using high pressures the pressure is kept always constant at 1 atmosphere and it was only raised to 2 atm during leakage tests.

The temperature in the experiments goes from 210ºC to 250ºC. Higher temperatures were not recommended since the copper could start to migrate and either form aggregations or be dragged with the gases out the reactor to the ventilation.
An important thing to take into account is the moment where the catalyst is fully activated. As it was observed before, the catalyst is not fully activated during the first cycle. The copper is partially reduced after the activation (section 2.5.1) and this can be seen on the amount of chlorine reacted during the first step. For this reason the first cycles are never taken into account in the calculations but their data is displayed so the issue just explained can be checked.

Table 3.1 List of experiments and their experimental conditions

Set number (code)	Cycle	total flow step 1 (ml/s)	PC_2H_4 (atm)	total flow step2 (ml/s)	PO_2 (atm)	T (K)	w_{Cu} (g_{Cu}/g_{cat})	m_{cat} (g_{cat})
1 (6_x)	1	1,512	0,100	0,77	0,301	523	5,77	0,565
	2	1,512	0,100	0,77	0,301			
	3	1,787	0,085	1,04	0,223			
	4	2,062	0,073	1,31	0,177			
	5	2,337	0,065	1,58	0,147			
	6	1,512	0,100	0,77	0,301			
2 (9_x)	1	1,787	0,085	0,74	0,633	508	5,77	0,437
	2	1,787	0,085	0,74	0,633			
	3	2,062	0,073	0,50	0,463			
	4	2,337	0,065	0,77	0,301			
	5	2,612	0,058	1,04	0,223			
3 (10_x)	1	2,612	0,058	1,04	0,223	493	6,11	0,732
	2	2,612	0,058	1,04	0,223			
	3	2,337	0,065	0,77	0,301			
	4	2,062	0,073	0,50	0,463			
	5	1,787	0,085	0,74	0,633			
4 (11_x)	1	-	-	1,17	1,000	483	6,11	0,498
	2	1,512	0,100	0,47	1,000			
	3	1,787	0,085	0,74	0,633			
	4	2,062	0,073	1,01	0,463			
	5	2,337	0,065	1,28	0,365			
5 (12_x)	1	-	-	1,44	0,812	523	6,11	0,490
	2	2,062	0,073	1,31	0,177			
	3	2,062	0,073	1,31	0,177			
	4	2,062	0,073	1,31	0,177			
	5	2,337	0,065	1,58	0,147			
	6	2,337	0,065	1,58	0,147			
	7	2,337	0,065	1,58	0,147			
	8	2,337	0,065	-	-			
6 (13_x)	1	1,512	0,100	1,04	0,223	493	6,11	0,556
	2	1,512	0,100	1,04	0,223			
	3	1,512	0,100	1,04	0,223			
	4	1,512	0,100	1,04	0,223			
	5	1,512	0,100	1,04	0,223			
	6	1,512	0,100	1,04	0,223			
	7	1,512	0,100	1,04	0,223			
7 (14_x)	1	-	-	1,17	1,000	483	6,11	0,526
	2	1,512	0,100	0,77	0,301			
	3	1,787	0,085	1,04	0,223			
	4	2,062	0,073	1,31	0,177			
	5	2,337	0,065	1,58	0,147			
	6	2,062	0,073	1,31	0,177			
	7	2,612	0,058	-	-			

Table 3.1 List of experiments and their experimental conditions (continues).

Set number (code)	**Cycle**	**total flow step 1 (ml/s)**	**PC_2H_4 (atm)**	**total flow step2 (ml/s)**	**PO_2 (atm)**	**T (K)**	**w_{Cu} (g_{Cu}/g_{cat})**	**m_{cat} (g_{cat})**
8 (18_x)	1	-	-	0,77	0,301	523	3,82	0,335
	2	1,512	0,100	0,77	0,301			
	3	1,512	0,100	0,77	0,301			
	4	1,512	0,100	0,77	0,301			
	5	1,512	0,100	-	-			
9 (19_x)	1	-	-	0,77	0,301	523	3,82	0,360
	2	1,512	0,100	0,77	0,301			
	3	1,512	0,100	0,77	0,301			
	4	1,512	0,100	0,77	0,301			
	5	1,512	0,100	-	-			

In some experiments the reactants were injected through the reactor with longer or shorter times. This is the case of the experiments 18_x and 19_x whose more specific information can be found on the table 3.4.

Some other experiments were done without catalyst and are not listed in the table 3.1. In these experiments the reactor was loaded with support, inert or was empty. There was an experiment where the HCl line was directly injected to the MS bypassing all the other lines. These experiments were run mostly in order to know the HCl adsorption on the lines, support or MS capillary lines and will be described precisely later on.

The total flow in the table tells the flow of reactant plus inert that is flowing through the reactor in each step.

From this point on, the experiments will be referenced by using the "code" written in brackets on the "Set number" column. The "x" is then substituted by the cycle number. As an example, the experiments 14_3 are the experiments done in the third cycle of the set number 7.

Table 3.2 Amount of chlorine and CuCl reacted in each experiment.

Experiment code	**Chlorine uptake (mol Cl/g_{Cu})**	**CuCl reacted (mol CuCl/g_{Cu})**	**P C_2H_4 (atm)**	**P O_2 (atm)**
6_1	0,00462	0,01672	0,100	0,301
6_2	0,01121	0,01264	0,100	0,301
6_3	0,00929	0,01097	0,085	0,223
6_4	0,00941	0,01166	0,073	0,177
6_5	0,01008	0,01164	0,065	0,147
6_6	0,00814	0,01002	0,100	0,301
9_1	0,00301	0,03641	0,085	0,633
9_2	0,00882	0,01932	0,085	0,633
9_3	0,01065	0,01023	0,073	0,463
9_4	0,01071	0,01133	0,065	0,301
9_5	0,00963	0,02064	0,058	0,223

Table 3.2 Amount of chlorine and CuCl reacted in each experiment (continues).

Experiment code	**Chlorine uptake (mol Cl/g_{Cu})**	**CuCl reacted (mol CuCl/g_{Cu})**	**P C_2H_4 (atm)**	**P O_2 (atm)**
10_1	0,00165	0,02643	0,058	0,223
10_2	0,00594	0,02709	0,058	0,223
10_3	0,00760	0,01352	0,065	0,301
10_4	0,00760	0,00948	0,073	0,463
10_5	0,00731	-	0,085	0,633
11_1	-	-	-	1
11_2	0,01015	-	0,100	1
11_3	0,00904	-	0,085	0,633
11_4	0,00801	0,00956	0,074	0,463
11_5	0,00701	0,01086	0,065	0,365
12_1	-	-	-	0,812
12_2	0,00868	0,01793	0,0737	0,177
12_3	0,00782	0,02368	0,0737	0,177
12_4	0,00708	0,01202	0,0737	0,177
12_5	0,00733	-	0,0651	0,147
12_6	0,00456	0,01336	0,0651	0,147
12_7	0,00754	0,01153	0,0651	0,147
12_8	0,00906	-	0,0651	-
13_1	0,00878	-	0,100	0,223
13_2	0,01022	0,02388	0,100	0,223
13_3	0,00960	0,01202	0,100	0,223
13_4	0,00916	0,01156	0,100	0,223
13_5	0,00472	0,00920	0,100	0,223
13_6	0,00796	0,01290	0,100	0,223
13_7	0,00823	0,00844	0,100	0,223
14_1	-	-	-	1,000
14_2	0,00765	0,01901	0,100	0,301
14_3	0,00723	0,01920	0,085	0,223
14_4	-	0,01318	0,073	0,177
14_5	0,00795	0,01072	0,065	0,147
14_6	0,00775	0,01282	0,073	0,177
14_7	0,00739	-	0,058	-
18_1	-	0,00000	-	0,301
18_2	0,00808	0,02426	0,1	0,301
18_3	0,01166	0,03808	0,1	0,301
18_4	0,00977	0,03553	0,1	0,301
18_5	0,00883	-	0,1	-
19_1	-	0,00000	-	0,301
19_2	0,00803	0,02153	0,1	0,301
19_3	0,00871	0,02218	0,1	0,301
19_4	0,00967	0,02196	0,1	0,301
19_5	0,00960	-	0,1	-

In some cells in the table above there are no data. In most of the times this is because the experiment wasn't performed, as the first step of the first cycle or the second step of the last cycle in some sets. Another reason is that the data wasn't good enough to be used. This is the case of the experiments where the partial pressure of oxygen was too high, the blank from the inert gas was useless and no data could be got from that.

3.2. First cycle discarding

In all the experiments done there's an observable less amount of chlorine reacted during the first ethylene chlorination step. This means that either the catalyst is not fully activated or some of the copper is already reduced to Cu^+.

Comparing the uptake chlorine in the different cycles it seems that after the first cycle the reacted chlorine rises. The opposite trend is seen in the amount of oxidized CuCl. In the first cycles it shows a higher amount of CuCl reacted. There's evidence then to believe that right after the activation process of the catalyst the copper is not completely reduced.

This leads to the discarding of the first cycle of each set of experiments, but sometimes one cycle is not enough to get the catalyst ready. As an example, in the experiment 10_2 the amount of chlorine is still low compared with later cycles in the same set of experiments; it has to be ensured that the data used afterwards for the kinetic fitting comes from experiments where the catalyst is fully activated.

This problem is not only observed in the fresh catalyst. After the experiments 12_5 and 13_4, the setup was shut down and the oven temperature was cooled down to room temperature for **12** and **36 hours** respectively. During this time the catalyst was not removed from the reactor.

After that time, the oven was heated again to the experiment temperature and the next experiments from each set were performed. During this part no activation process was done, the only moment where the catalyst was treated was right before the experiments 12_1 and 13_1.

The results (see 12_6, 12_7, 12_8 and 13_5, 13_6, 13_7) showed that, again, there was a lower amount of chlorine reacted at the beginning and the amount increases as it does during the first experiments with a fresh catalyst. Despite this fact, the reacted CuCl results show a different behavior in the second step.

The amount of CuCl reacted during the first cycle of an experiment with fresh catalyst show a higher uptake compared with the cycles which come next. This can be explained by the higher amount of reduced copper in the catalyst, but in this case is different. The CuCl reacted after the experiments 12_5 and 13_4 is not that high even though the chlorine reacted is lower so that's the proof that the catalyst needs to be treated again like a fresh catalyst in order to recover the activity. This leads to think that the experiments have to be planned and done in a row since the time spent during the start up, the activation and the first unusable cycles is quite high and the experiments have to be done continuously because as it is explained, the catalyst needs to be activated if the temperature is lowered for a relative short period of time.

3.3. Catalyst activation

In the section 2.5.1. the two different activation methods are explained. Here the results obtained from both methods will be discussed and it will be decided which one works better and leads to a faster activation of the catalyst.

The main difference between both methods is the cycle in which the experiments are started. In the first method the ethylene chlorination is the first cycle run and in the second method the first cycle run is the oxidation for a little bit longer time than usual (around **40 minutes** with O_2 flow).

Table 3.3 Comparison between first (left) and second (right) activation methods.

Exp. code	Chlorine uptake (mol Cl/g_{Cu})	CuCl reacted (mol CuCl/g_{Cu})	Exp. code	Chlorine uptake (mol Cl/g_{Cu})	CuCl reacted (mol CuCl/g_{Cu})
6_1	0,00462	0,01672	11_2	0,01015	-
6_2	0,01121	0,01264	12_2	0,00868	0,01793
9_1	0,00301	0,03641	14_2	0,00765	0,01901
9_2	0,00882	0,01932	18_1	-	0,00000
10_1	0,00165	0,02643	18_2	0,00808	0,02426
10_2	0,00594	0,02709	19_1	-	0,00000
13_1	0,00878	-	19_2	0,00803	0,02153
13_2	0,01022	0,02388	19_3	0,00871	0,02218

It is obvious that the chlorine uptake during the first cycle is very low because on what is explained in the section 3.2. For an easier comparison between both methods four plots are showed below. In these figures the chlorine uptake was plotted versus the cycle of the experiment and the same s done for the second step and the reacted CuCl.

The experiments are done at different temperatures and partial pressures. The temperature and partial pressure of the experiments show no observable dependence on how fast the catalyst activates completely, the absolute value of the uptake chlorine might depend on it, but this won’t be discussed in this section.

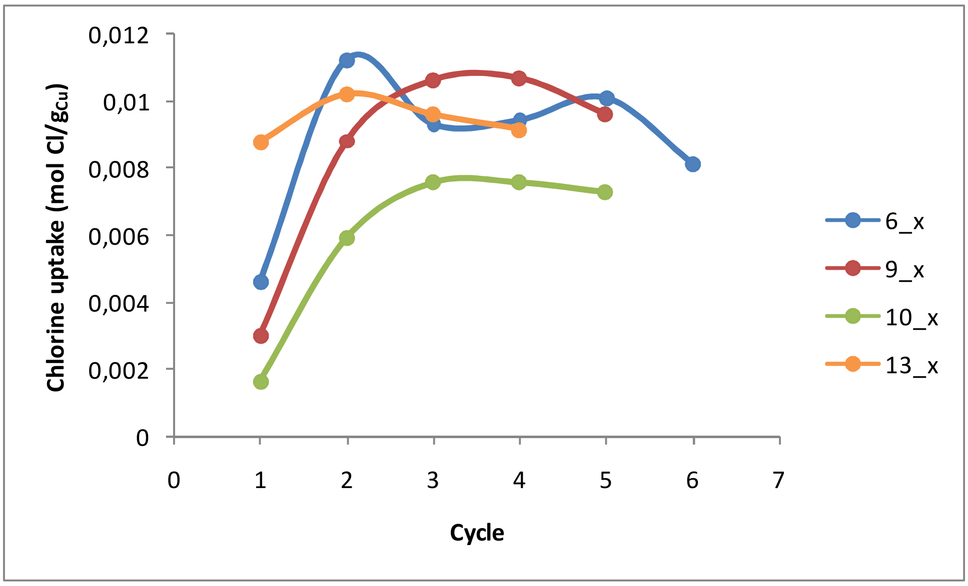


Figure 3.1 Amount of chlorine uptake on every cycle for all the experiments starting with the ethylene chlorination step. Temperatures of each set of experiments 6_x, 9_x, 10_x and 13_x are respectively **T**= 523K, 508K, 493K and 493K.

In the set 9_x and 10_x the catalyst is not completely activated yet in the second cycle. The influence of the partial pressure is discarded because as shown in the table 3.2, the partial pressure of ethylene in 9_x is decreased in further cycles and for the set 10_x it's just the opposite so there's no reason to think that the partial pressure of ethylene in the very first cycles affects the activation of the catalyst.

The temperature in the first experiments doesn't seem to activate faster the catalyst, but it's important to remember that all experiments had the activation step at 493K. Looking at the figures 3.1 and 3.2 there's no evidence that the experiments temperatures take part on how fast the catalyst becomes fully activated.

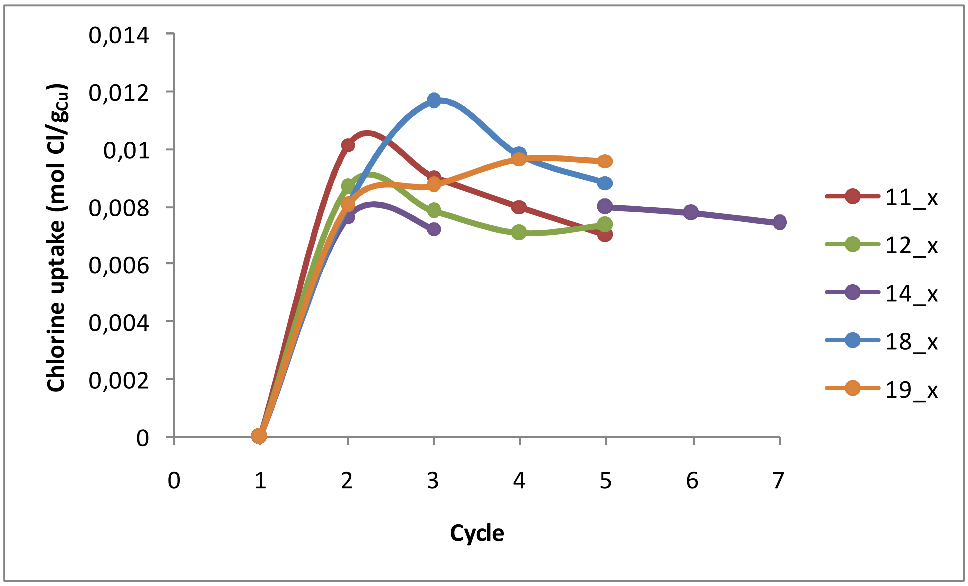


Figure 3.2 Amount of chlorine uptake on every cycle for all the experiments starting with the oxidation step. Temperatures of each set of experiments 11_x, 12_x, 14_x, 18_x and 19_x are respectively **T**= 483K, 523K, 483K, 523K and 523K.

Comparing the figures 3.1 and 3.2 it's observed that in more cases the catalyst is completely activated on the second cycle. However, in both methods there are experiments where the second cycle is not useful, as the 9_2, 10_2 and 18_2. There is only one experiment out of five in the figure 3.2 where the second cycle is discarded, compared with the figure 3.1 it seems that the likelihood for the catalyst not to be fully activated on the second cycle is higher for the first method.

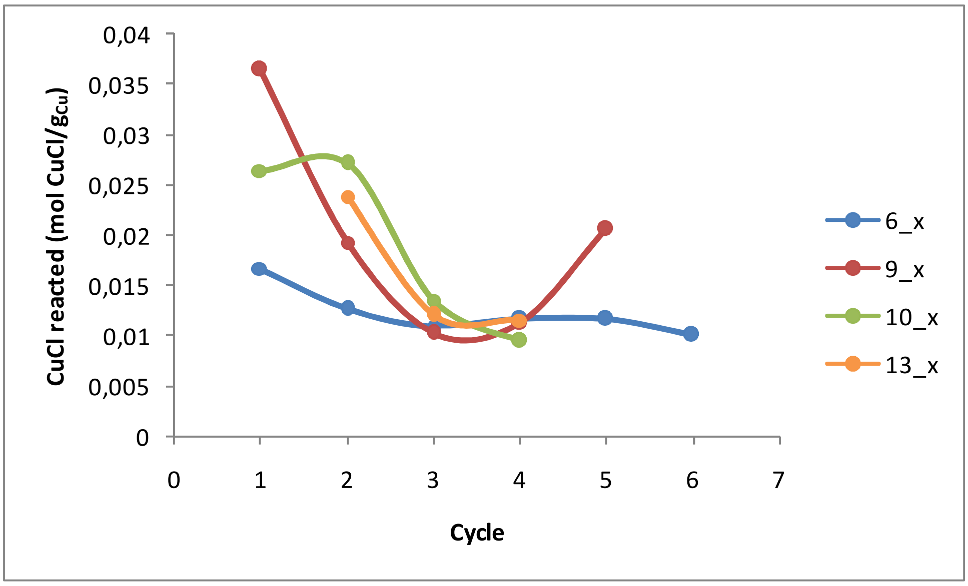


Figure 3.3 Amount of CuCl reacted on every cycle for all the experiments starting with the ethylene chlorination step. Temperatures of each set of experiments 6_x, 9_x, 10_x and 13_x are respectively **T**= 523K, 508K, 493K and 493K.

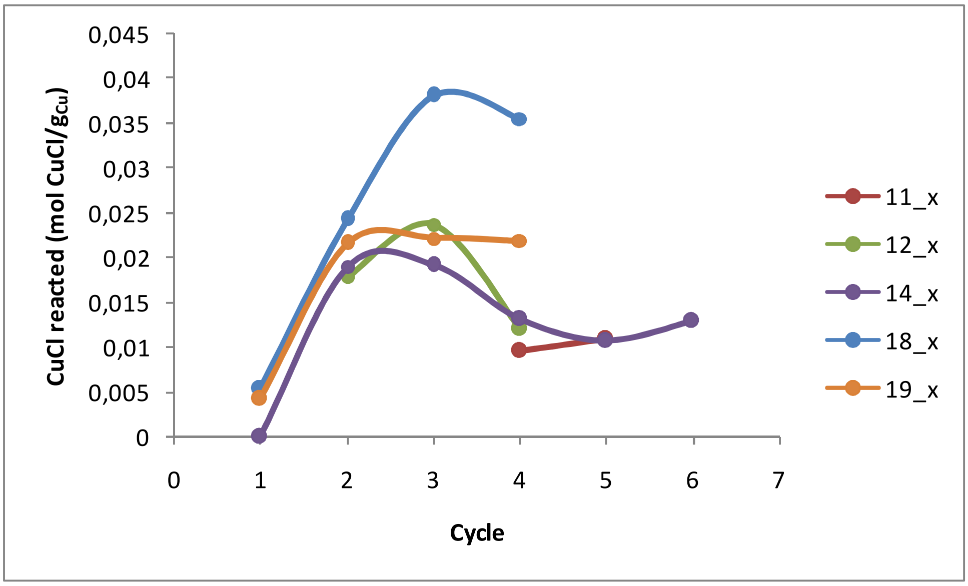


Figure 3.4 Amount of CuCl reacted on every cycle for all the experiments starting with the oxidation step. Temperatures of each set of experiments 11_x, 12_x, 14_x, 18_x and 19_x are respectively **T**= 483K, 523K, 483K, 523K and 523K.

The amount of CuCl reacted during the first cycle is much higher in the figure 3.3 than in the 3.4. The reason for that is because in the first method the ethylene chlorination is run before the second step, this causes the copper to reduce and therefore the amount of CuCl to be oxidized in the second step is much higher. Moreover the amount of reduced copper in the fresh catalyst is very low.

In the second method the only CuCl reacted comes from the CuCl present in the fresh catalyst.

In the second cycle the amount of CuCl for both methods lay in a similar range but in the third cycle the CuCl reacted in the first method keeps decreasing and the catalyst seems to be activated for both methods.

Then, the reason why the chlorine uptake during the first step in the first cycle is too low is not so clear. At first it was believed that the copper was partially reduced and that might cause the low conversion to EDC. The fact is that the CuCl reacted amount is quite low on the second method (where the very first cycle run is the oxidation) and that discards the possibility for the copper to be partially reduced just after the activation.

The possibility that could explain this is that the catalyst might be oxidized during its preparation in contact with the air and the amount of chlorine in the catalyst is lower than the expected.

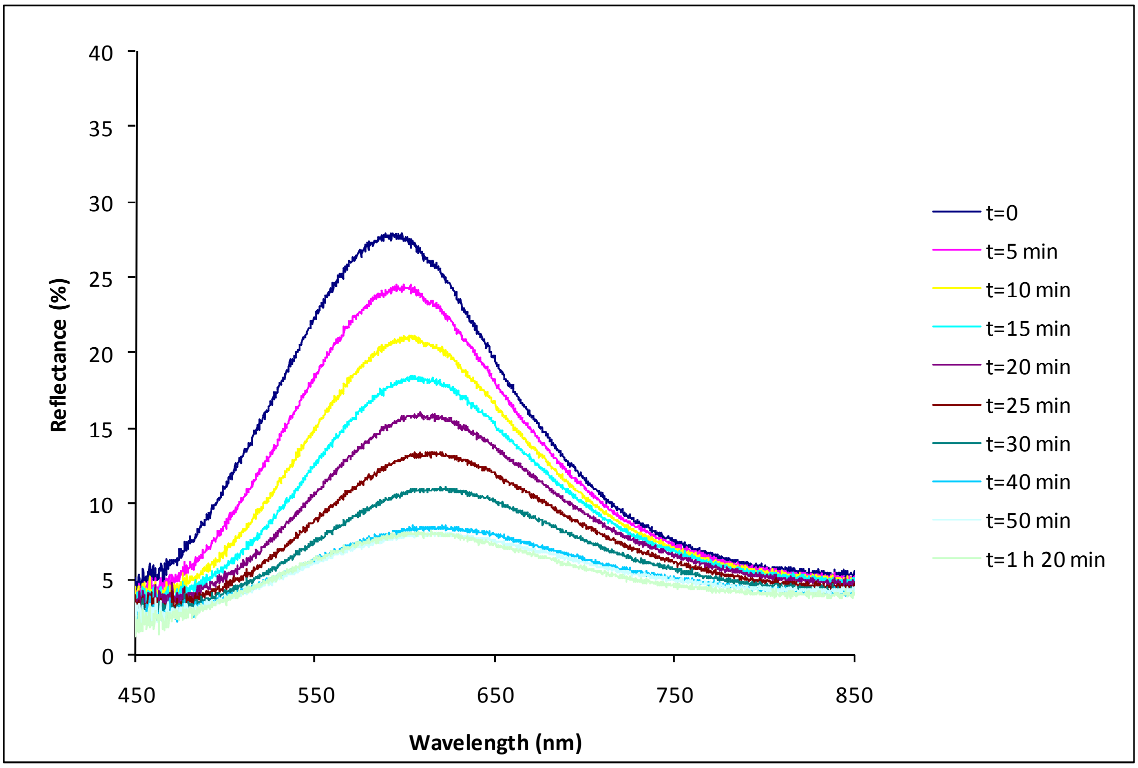


Figure 3.5 UV-vis spectra during the pretreatment activation process of the catalyst. **T**=493K Helium flow of 3ml/s.

When the catalyst is loaded in the reactor it is partially hydrated. This can be known only by seeing the color of the catalyst; it is normally greenish when it’s being loaded to the reactor most probably because of the contact with the ambient moisture. Some minutes of direct contact with the atmosphere is enough to see the color change.

One of the reasons of the pretreatment, besides the catalyst activation, is the removal of the water from the catalyst. When the catalyst is dehydrated it turns into a brown color.

The spectra in the figure 3.5 show how the reflectance of the catalyst drops along the pretreatment. This is mainly because of the water removal from the catalyst. At the end of the pretreatment the spectra looks very close both in shape and maximum peak value to the spectra corresponding to the end of the third step.

3.4. Catalyst deactivation

Some experiments were done in order to study the reproducibility of the catalyst. Three sets of experiments were done at different temperature and partial pressure of reactant so the deactivation of the catalyst can be observed depending on three parameters: temperature of reaction, partial pressure and cycle.

Two more experiments were done with the goal to figure out which was the step where the deactivation was predominant. In the table 3.4 there are the information of how long the reactants were flowing through the reactor on each step.

The figures 3.6 and 3.7 show the chlorine and CuCl reacted during their respective step.

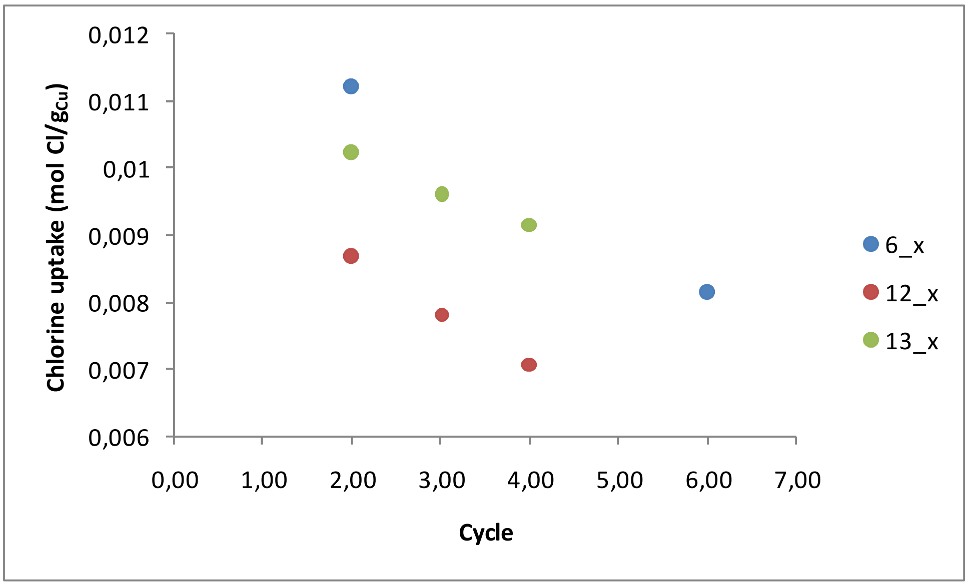


Figure 3.6 Amount of chlorine reacted on every cycle for all the experiments where the catalyst deactivation was studied. The operation conditions of the experiments 6_x, 12_x and 13_x were respectively; **PC_2H_4** = 0.100 atm, 0.0737 atm and 0.100 atm; **T** = 523K, 523K and 493K.

In the set of experiments 6_x only the first and last cycle could be used for the catalyst deactivation study because the other cycles were performed at different partial pressures of ethylene and oxygen. In this case the results are quite clear, there's a noticeable deactivation of the catalyst cycle after cycle. The experiments 6_x and 13_x were performed at higher partial pressure than the experiments 12_x and it is reflected as a higher chlorine uptake.

However, it doesn't seem that the partial pressure of ethylene affects the deactivation if the experiments 6_x and 12_x are compared since both have the same operation temperature. Both experiments show a linear deactivation and are parallel; the slopes of the three experiments were calculated in order to compare easily the data. For the experiments 6_x and 12_x the slope is **$-7.68\cdot10^{-4}$** and **$-8.00\cdot10^{-4}$** while the slope for the experiments 13_x is **-5.30·10^{-4}**. Then it seems that the partial pressure only affects the absolute value of the chlorine uptake but is not implied in the catalyst deactivation rate.

The temperature effect on the deactivation can be studied by comparing the experiments 6_x and 13_x. Both experiments were performed at the same partial pressure of ethylene and at the temperature of **523K** and **493K** respectively. The deactivation rate is higher for higher temperatures as expected. A deeper study could be done by studying the deactivation rate of the catalyst at different temperatures and see what kind of dependence has the temperature with the deactivation rate.

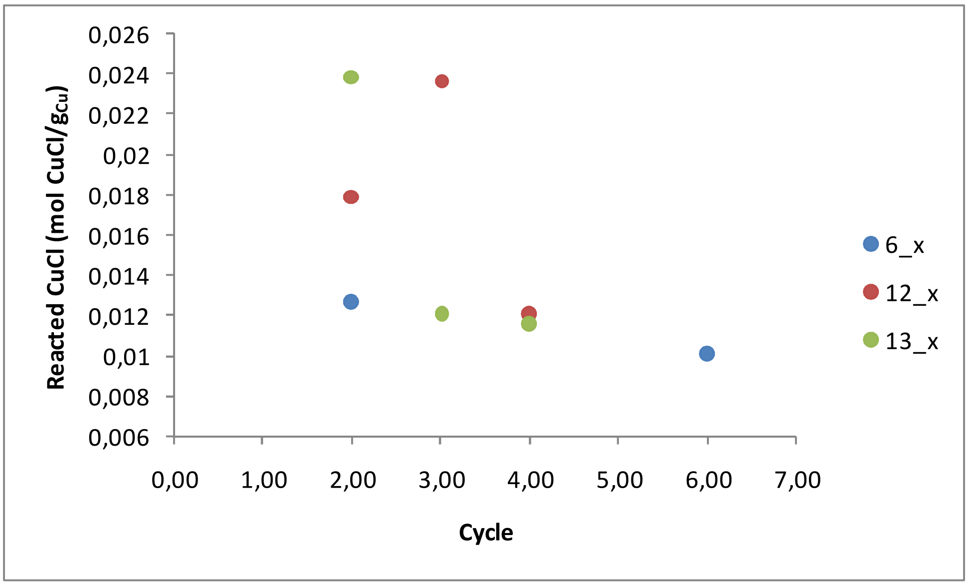


Figure 3.7 Amount of CuCl reacted on every cycle for all the experiments where the catalyst deactivation was studied. The operation conditions of the experiments 6_x, 12_x and 13_x were respectively; **PO$_2$** = 0.301 atm, 0.177 atm and 0.233 atm; **T** = 523K, 523K and 493K.

Unfortunately the results are not so clear on the second step. The reacted CuCl should be around 0.012 or lower but it seems that in the early cycles of some experiments the consumed oxygen is a bit higher.

In the table below the times of each step in the experiments 18_x and 19_x are displayed. By doing the experiments with different times it s expected to see some changes in the deactivation. Therefore the experiments with higher deactivation could be related to the longer time in a specific step, which means that the mentioned step had more influence in the catalyst deactivation than the other two.

Table 3.4 Time on stream of the different steps of the experiments 18_x and 19_x.

Experiments\step	Ethylene chlorination	Oxidation	Catalyst chlorination
18_x	20-30 min	20-30 min	60 min
19_x	20-30 min	60 min	10-15 min

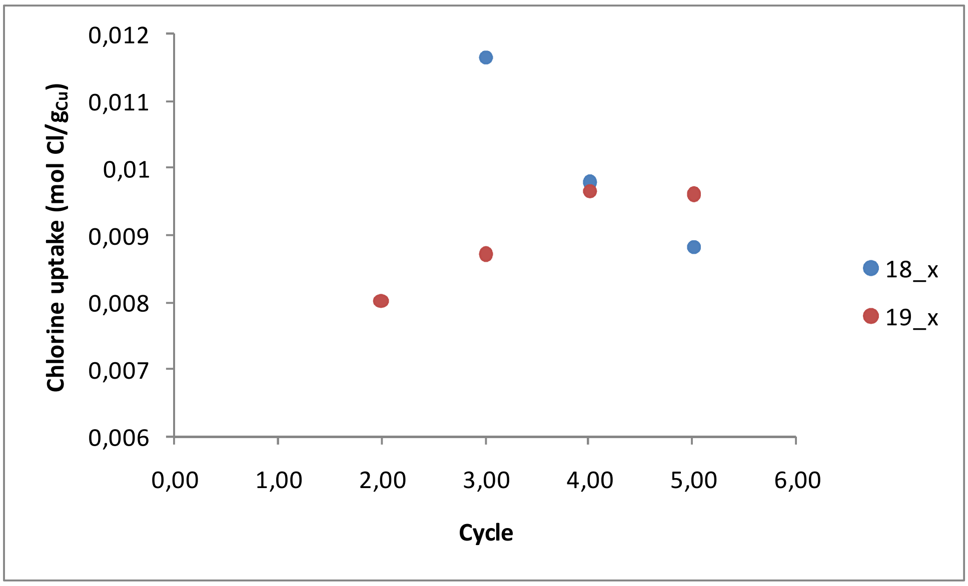


Figure 3.8 Amount of chlorine reacted on every cycle for all the experiments where the catalyst deactivation was studied. The operation conditions of the experiments 18_x and 19_x were the same; **PC_2H_4** = 0.100 atm; **T** = 523K. The amount of time under a constant reactant flow was higher (1 hour) on the step 2 on the experiments 19_x and higher (1 hour) on the step 3 on the experiments 18_x.

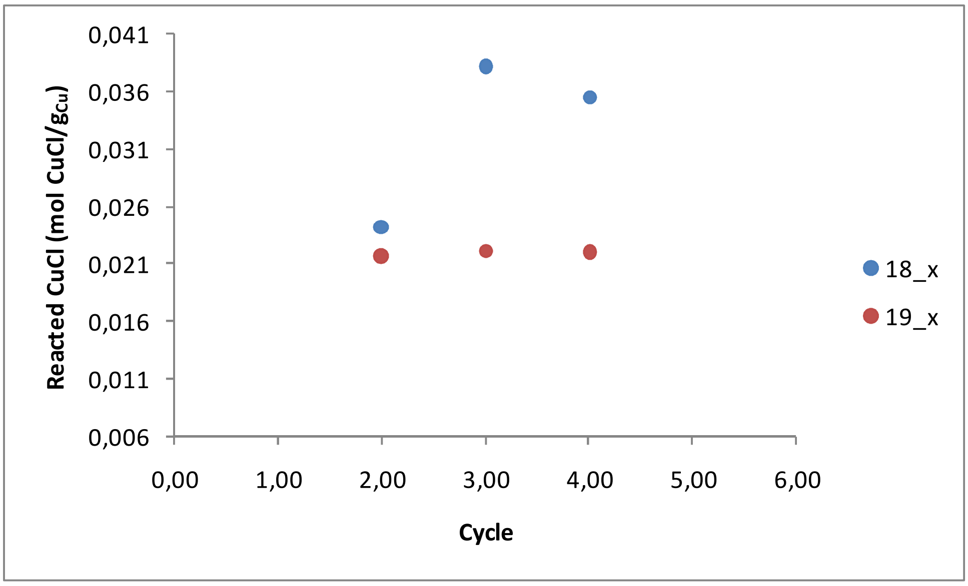


Figure 3.9 Amount of chlorine reacted on every cycle for all the experiments where the catalyst deactivation was studied. The operation conditions of the experiments 18_x and 19_x were the same; **PO_2** = 0.301 atm; **T** = 523K. The amount of time under a constant reactant flow was higher (1 hour) on the step 2 on the experiments 19_x and higher (1 hour) on the step 3 on the experiments 18_x.

The results in the chlorine uptake are quite clear. The experiments where higher times were used for the third step (experiments 18_x) show a decrease in the chlorine uptake cycle after cycle as seen in the experiments from the figure 3.6. On the other hand there’s no observable deactivation in the experiments 19_x where the long step was the oxidation.

Comparing the slope of the experiments 18_x with the value of **$-1.42\cdot 10^{-3}$** [mol Cl/(g_{Cu} · Cycle)] with the experiments 6_x or 12_x, there's a clear difference and in the experiment 18_x the deactivation is faster, probably because of the longer time on the third step.

The experiments 19_x show a completely opposite behavior, the catalyst not only does not seem to deactivate but its activity seems to increase. There's the possibility that the catalyst is not fully activated but this is rather a remote chance because in all the experiments the catalyst was activated on the third cycle. Moreover the reacted CuCl is constant after the second cycle.
In that experiment it was important the lower time during the third step and 15 minutes are enough to rechlorinate the catalyst.

3.5. HCl adsorption study

Since the beginning the HCl was a problematic compound during the experiments. There were many troubles to get reliable data from the third step, that's why there's almost no data from this step in the results. Only in the latest experiments it was decided to use the pH-meter after all the experiments related with the HCl adsorption.

One of the problems that had to be faced was the HCl adsorption on the lines. There was a strong delay in the MS data before the signal of HCl started to rise. There were many places where the HCl could be adsorbing so many experiments were done in order to have a better idea.
In these experiments, the HCl was being injected through different parts of the set up and then in the MS, this would provide information of where the delay times where longer and therefore the adsorption stronger. Finally it came out that all the experiments had a long delay time and it was supposed that the HCl could be adsorbing also in the capillary lines of the MS.

In the figure below the plot show the ion intensity corresponding to the HCl amount in the MS. That is the experiment where the HCl was injected directly to the MS from the gas bottle

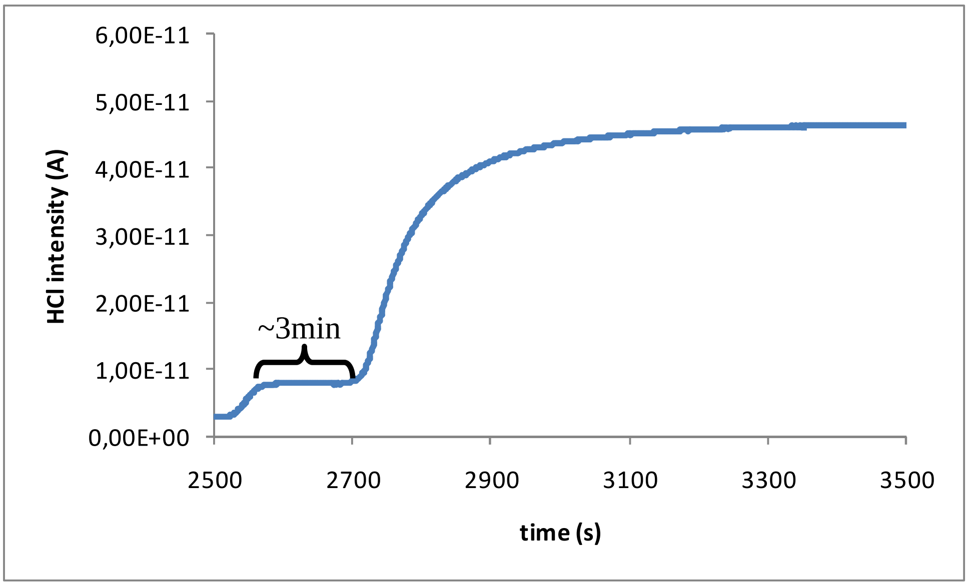


Figure 3.10 Amount of HCl recorded in the MS direct from flow which bypassed all the valves, lines and reactor. $\mathbf{P_{HCl}}$ = 0.05 atm; molar flow ~ $3.22\cdot10^{-6}$ mol_{HCl}/s.

Then it's clear that the MS cannot be used to record the HCl amount in the third step and the pH-meter is used instead.

The pH is directly measured from a solution of **2 liters** of distilled water. The flask where the water was contained was under stirring and the line which connected the reactor outlet with the MS was unattached and sunk in the flask so the reactor outlet stream could be bubbled in the solution.

Before proceeding with the experiments a test was made to check that all the HCl bubbled was being absorbed in the water and nothing was going through the water and being dispersed in the laboratory. Since the flow and purity of HCl was known it was easy to compare the theoretical amount of HCl that should be absorbed with the experimental one.

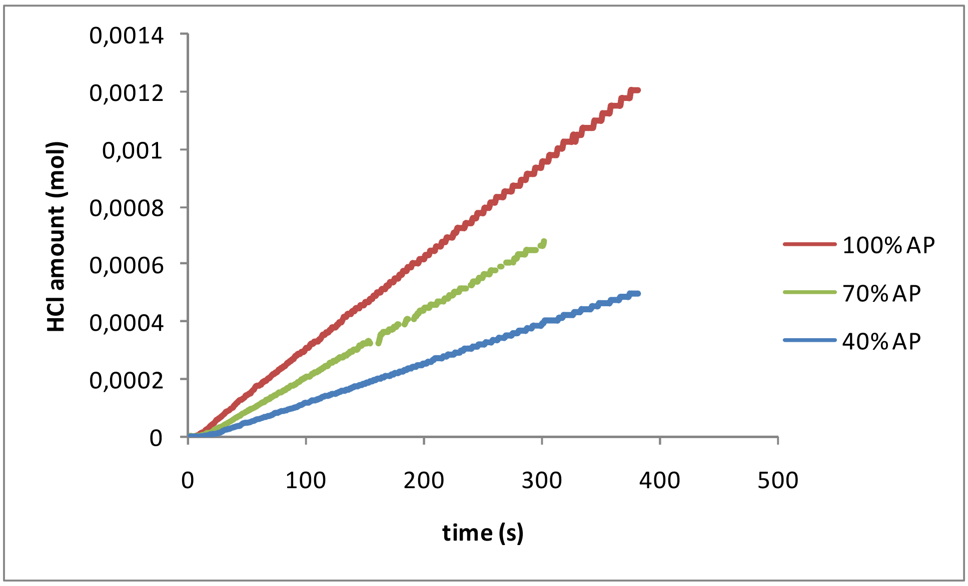


Figure 3.11 Blank experiments for the HCl absorption in the distilled water.

The table 3.5 shows the slope from the experiments in the figure 3.11, which corresponds to the flow of HCl absorbed in the water solution. The flow calculated in the corresponding MFC for the HCl might have some error, for this reason the theoretical flow is a bit lower than the flow absorbed in the solution. Anyway this means that the water amount can uptake all the HCl from the stream that is being bubbled.

Table 3.5 Theoretical and experimental results for the HCl blank experiments.

HCl % AP	HCl theoretic flow (mol/s)	HCl experimental flow (mol/s)
100	2,83E-06	3,22E-06
70	1,98E-06	2,31E-06
40	1,13E-06	1,38E-06

After checking that the pH-meter could record all the HCl from the outlet reactor stream some experiments were done.

First an experiment with empty reactor was made in case some HCl was being adsorbed on the lines. The other experiments could be referenced to this one in order to discard the HCl adsorbed in the lines from the total HCl consumed.

Another experiment with only support was also made. In this case the amount of support used for this experiment had to be the same that the corresponding support mass in the catalyst from an experiment with reaction. It is not clear whether the presence of $CuCl_2$ over the support affects the HCl adsorption on the support, but it’s supposed that the change in the adsorbed HCl won’t be much different.

One last experiment is also needed with catalyst. With this experiment we can know the total amount of HCl reacted and adsorbed to the lines and support. Since we have the experiment with only support at the corresponding support mass in the catalyst we can make the difference to know the real amount of HCl reacted.

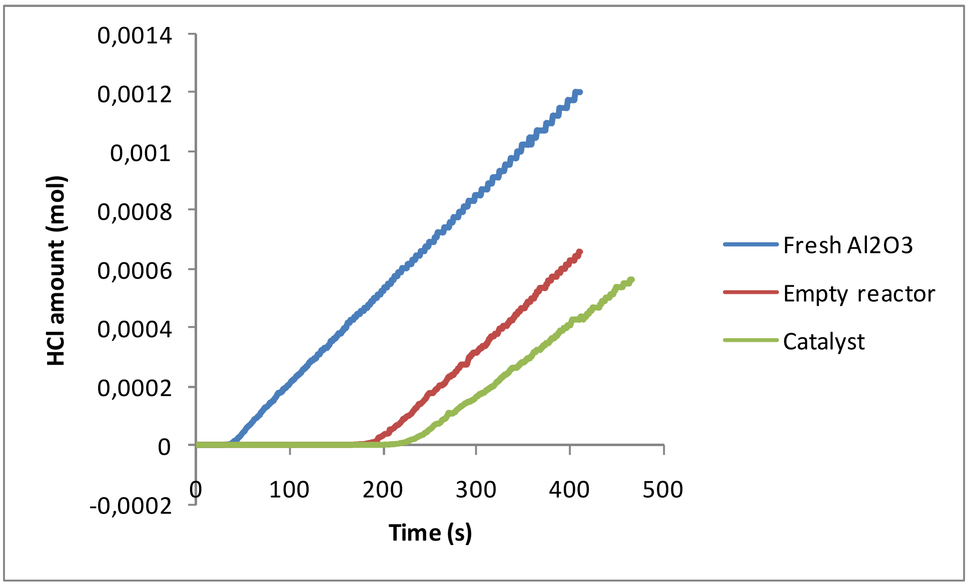


Figure 3.12 Amount of HCl measured in a 2 liter solution of distilled water at the reactor out stream with pH-meter. The experimental conditions for all three experiments were **T** = 483K and $\mathbf{P_{HCl}}$ = 0.05 atm; molar flow ~ $3.22\cdot 10^{-6}$ mol_{HCl}/s.

In the figure 3.12 the data from these experiments is shown. These are the concentration profiles recorded and calculated (see section 2.3.4.) with the pH-meter. It makes sense how the experiment with the catalyst takes longer time to be detected by the pH-meter than the experiment with support because of the HCl reacted. The same happens between the experiments with support and the experiment with empty reactor.

It's also important the fact that in both experiments with support and catalyst the HCl is completely consumed either by the adsorption or the reaction. This makes really hard to know the kinetic information of the reaction because the HCl flow is detected only when the reaction/adsorption is almost completed.

The good side is that at least the amount of HCl consumed can be calculated by comparing the different experiments done.

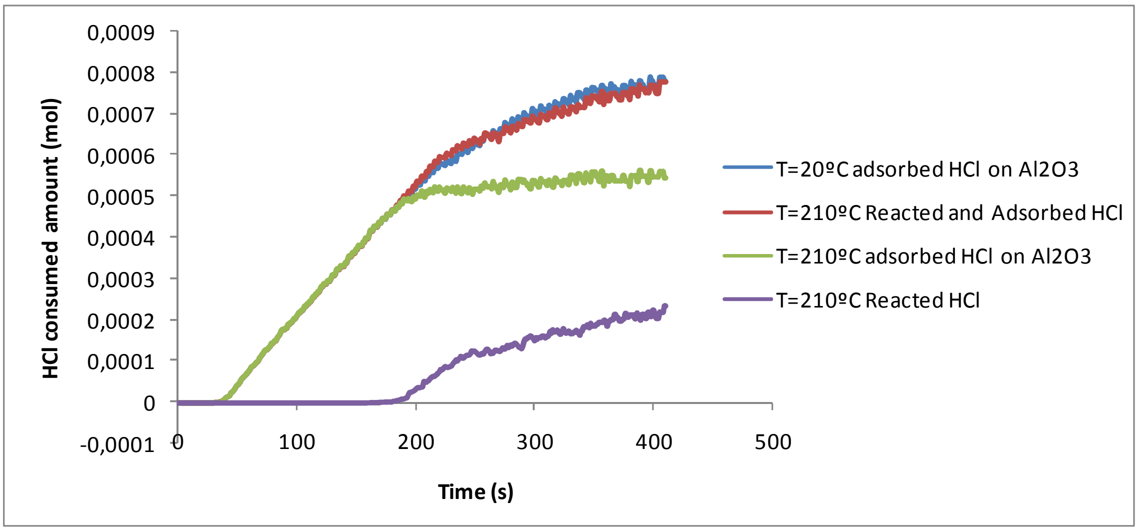


Figure 3.13 Amount of consumed HCl during different experiments measured with pH-meter. All the experiments were run at the same partial pressure: $\mathbf{P_{HCl}} = 0.05$ atm; molar flow ~ $3.22 \cdot 10^{-6}$ mol_{HCl}/s.

Using the data recorded from the experiments in the figure 3.12 and other similar ones at different temperatures, the amount of HCl consumed is calculated by subtracting the corresponding blank (empty reactor or support loaded reactor) from the experiments done with catalyst.

In figure 3.13 the plots show the different HCl consumed in the different experiments. An experiment with catalyst was referenced to the two different blanks; with the first blank, the one performed with the empty reactor, the overall amount of consumed is calculated (red line) and with the second blank, the one with the corresponding mass of support (green line), the amount of reacted HCl is calculated (purple line).

It seems that the adsorption on the support is stronger than the reaction of HCl, moreover from all the consumed HCl the **71.8%** is adsorbed on the catalyst surface and the rest **28.2%** is reacted with the Cu_2OCl_2.

During the experiments the HCl adsorbed on the support is removed afterwards, supposedly during the first step, in the section 3.6. there are more details about it. For sure the HCl is not so easily removed without the ethylene as explained in the following.

Two more experiments were done to compare the adsorption of HCl on the support when it's fresh and when it's already chlorinated. The first experiment was run with the fresh catalyst as in the experiments before, but then there was a step with only helium flow (~**2ml/s**) during **30 minutes** keeping the same temperature as in the test (483K). It was expected that most of the HCl would be desorbed during this step, but it wasn't. After this step, a second experiment was run in order to know how much HCl was adsorbed this time so it could be compared with the adsorbed HCl with the fresh catalyst.

The figure 3.14 show the difference between the first and the second test, the HCl starts to be detected by the pH-meter much sooner in the second test than in the first. In fact is really close to the blank done with the empty reactor which means that a few amount of HCl was adsorbed this time.

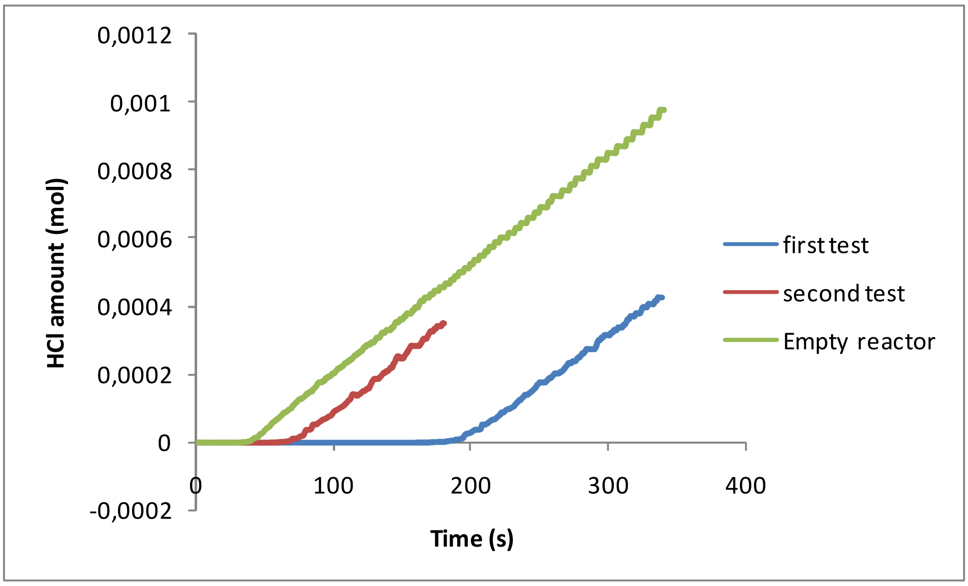


Figure 3.14 Amount of HCl measured in a 2 liter solution of distilled water at the reactor out stream with pH-meter. The experimental conditions for both experiments were **T** = 483K; $\mathbf{P_{HCl}}$ = 0.05 atm; $\mathbf{m_{sup}}$ = 0.466g; molar flow ~ $3.22 \cdot 10^{-6}$ mol_{HCl}/s.

The HCl adsorbed amount can be compared easily in the figure 3.15 where the two experiments were referenced to the experiment with the empty reactor. The amount of HCl adsorbed is around 5 times smaller in the second cycle which definitely leads to think that the HCl does not desorb from the support unless there's the catalyst present and ethylene is injected.

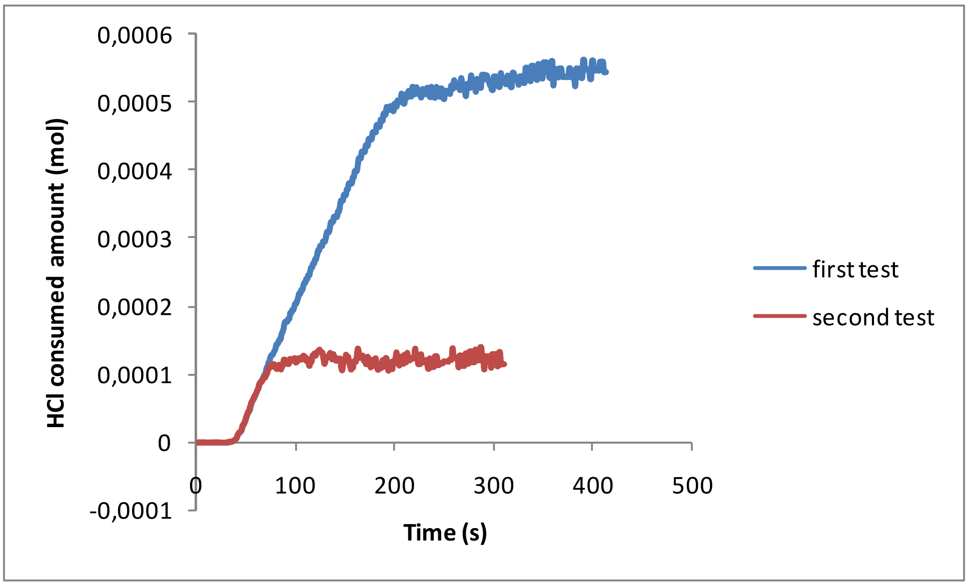


Figure 3.15 Amount of adsorbed HCl during different experiments measured with pH-meter. The experimental conditions for both experiments were **T** = 483K; $\mathbf{P_{HCl}}$ = 0.05 atm; $\mathbf{m_{sup}}$ = 0.466g; molar flow ~ $3.22 \cdot 10^{-6}$ mol_{HCl}/s.

Using the information from the first cycle, the amount of HCl adsorbed per mass of support at the experiment temperature is $\mathbf{1.165 \cdot 10^{-3}\ mol_{HCl}/g_{sup}}$.

3.6. HCl results with pH-meter

During the experiments 19_x the third step was recorded with the pH-meter for further data treatment. There's no blank with the corresponding mass of support for this experiment so the amount of reacted HCl is not known yet. Comparing the profiles differences between the figures 3.14 and 3.16 it seems that the HCl adsorbed on the support is removed after the first cycle, otherwise there would be a high difference between the first cycle and the rest of them and the last profiles would be much closer to the empty reactor blank curve.

In these experiments the mass of catalyst used was $\mathbf{0.360\ g_{cat}}$ so the amount of HCl adsorbed is not comparable with the experiments in the figure 3.14. The corresponding mass of support for this mass of catalyst is $\mathbf{0.334\ g_{sup}}$ so the adsorbed and reacted HCl in these experiments will be related to this number.

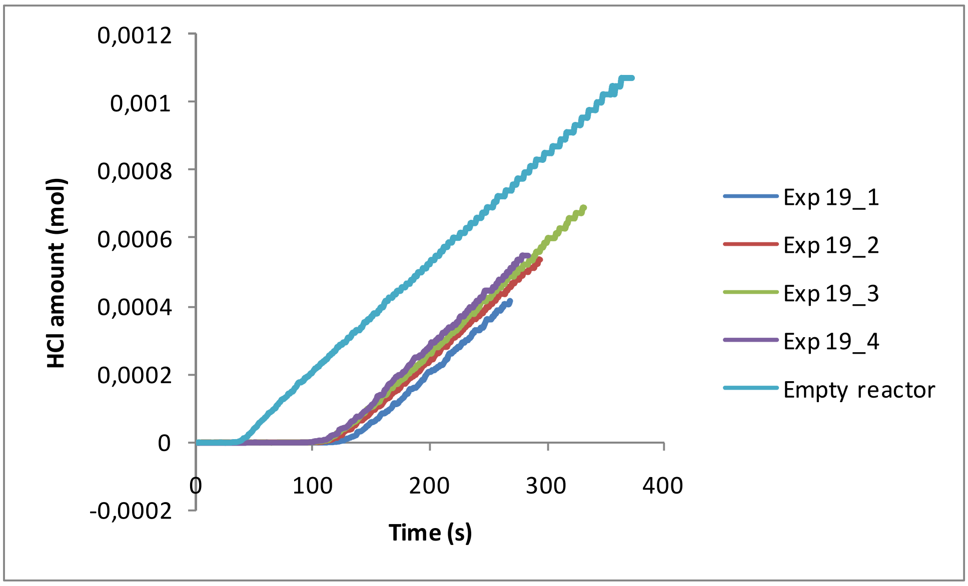


Figure 3.16 Amount of HCl measured in a 2 liter solution of distilled water at the reactor out stream with pH-meter. The experimental conditions for both experiments were **T** = 523K; $\mathbf{P_{HCl}}$ = 0.05 atm; $\mathbf{m_{cat}}$ = 0.360g; molar flow ~ $3.22 \cdot 10^{-6}$ mol_{HCl}/s.

The amount of adsorbed HCl decreases cycle after cycle. This is probably due to the catalyst deactivation, but it cannot be assured before a blank with support is recorded in order to calculate only the amount of reacted HCl. Even though the adsorbed HCl on the support is believed to be kept constant there's not enough information yet to be sure about this.

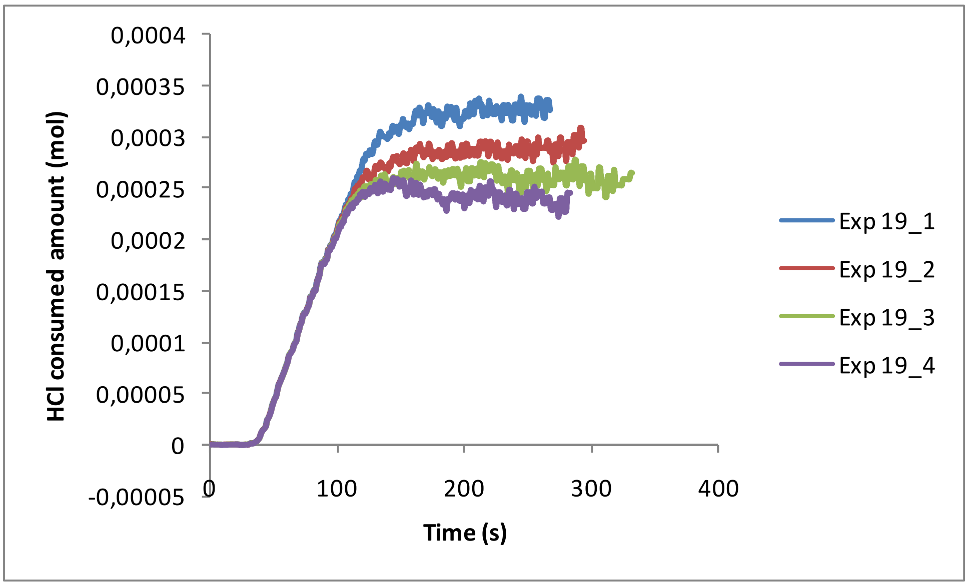


Figure 3.17 Amount of adsorbed HCl during different experiments measured with pH-meter. The experimental conditions for both experiments were **T** = 523K; $\mathbf{P_{HCl}}$ = 0.05 atm; $\mathbf{m_{cat}}$ = 0.360g; molar flow ~ $3.22 \cdot 10^{-6}$ mol_{HCl}/s.

The table 3.6 shows the relative HCl consumed during the experiments 19_x and the relative HCl adsorbed on the support in the first test of the figure 3.15. The HCl consumed during the experiments 19_x includes both support adsorption and reaction. From the experiments done before we know that the fraction of adsorbed HCl is much higher than the reacted HCl but we cannot calculate only the exact amount of adsorbed HCl.

Table 3.6 Consumed HCl in the experiments 19_x and the first test in figure 3.15.

	19_1	**19_2**	**19_3**	**19_4**	**Figure 3.15 test1**
HCl consumed (mol_{HCl})	3,26E-04	2,96E-04	2,65E-04	2,46E-04	5,43E-04
Relative consumed HCl (mol_{HCl}/g_{sup})	9,75E-04	8,86E-04	7,92E-04	7,37E-04	1,17E-03

3.7. MS and UV-vis synchronization

In all the experiments done, the MS data is started to be recorded **15 seconds** earlier than the UV-vis spectrometer and **30 seconds** earlier than the start of the experiment. The point is to synchronize both MS and UV-vis data and, after processing the data, try to compare the data and find a correlation between both recorded signals. The goal is to be able to know the amount of each of the copper formations in the catalyst only by checking the data from the UV-vis.

So far this has been done with the MS data, the amount of reacted ethylene or oxygen gave the information of how much copper had been reduced or oxidized during each step.

Three different fittings were done depending on the UV-vis data used in every case. For the MS it was used the EDC ion current recorded and the reacted CuCl amount for the first and second step respectively. The UV-vis main data source used is the Kubelka-Munk Function vs. photon energy plot and three different variables are taken into account to compare which one fits better with the MS data. These variables are the peak height of the peak at around **1.5eV**, the maximum value of the peak at around **3.5eV** and the Adsorption Edge Energy (AEE).

Unfortunately there were some troubles in the UV-vis data. There was an intense noise from at wavelengths lower than **400nm** which made impossible to get reliable information at photon energies higher than **2.6eV**. Therefore the peak around **3.5eV** could not be included and the maximum value of this peak could not be used for the fitting, but the closest value, which corresponds at the photon energy of **2.6eV**, is used instead.

In the first MS/UV-vis data comparison done the peak height around **1.5eV** has been used. In this case there were some troubles in the calculation when the peak was almost flat, due to some noise and the way of calculation there’s an increase of the peak value after **time: 500s** in the figure 3.18. At that point the peak height is constant along the rest of the experiment and almost zero, but it could not be corrected from the calculations.

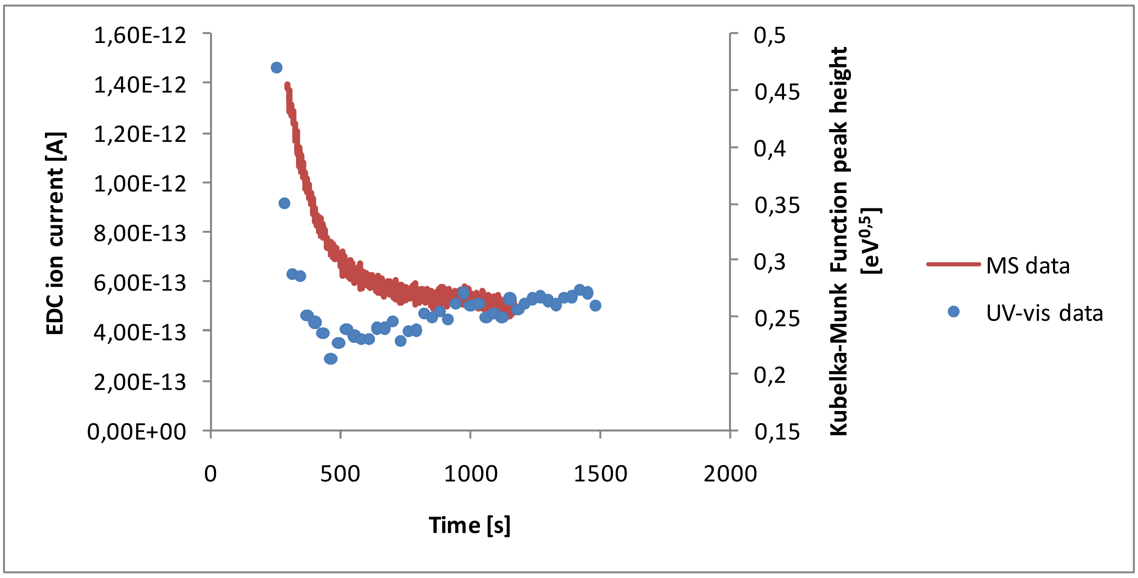


Figure 3.18 Intensity of the corresponding EDC ion in the MS and height of the peak at 1.5eV from the KM-function vs. photoenergy plot in the UV-vis. Data corresponding to the first step of the experiment 14_3. **T** = 483K; **PC_2H_4** = 0.085 atm.

Despite the noise after the **500s** it looks like the EDC correlates well with the peak height. Since the peak at **1.5eV** is more related to the Cu^{2+} it makes sense that the drop of the peak height and the EDC amount are so close.

The second step does not look so close as the first one. The change in the peak height is slower than the raise of the reacted CuCl. Comparing the figures 3.18 and 3.19 there's a significant difference between the maximum values of the peak height. In the first step the height is a little bit lower than **0.5 $eV^{0.5}$** but in the second step the peak keeps rising up to the value of **0.95 $eV^{0.5}$**.

After checking the spectra between experiments it was observed that when there was no oxygen flowing through the catalytic bed, the peak height decreased until it was stabilized in a lower value. Even though the reaction is almost over at time: **400s**, there might be some change in the catalyst surface that explains the late peak height stabilization.

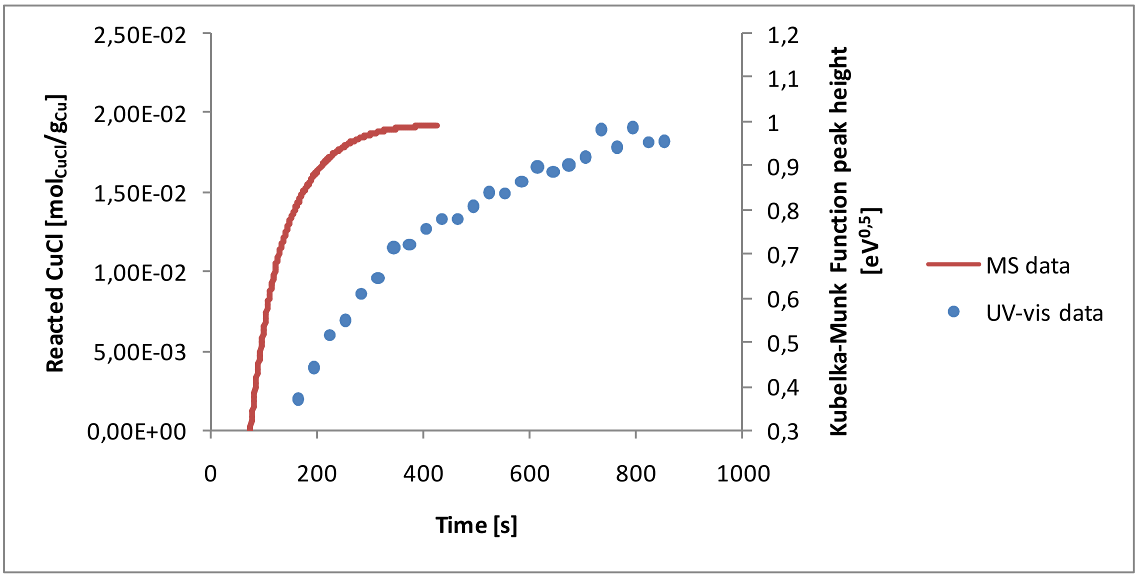


Figure 3.19 Calculated amount of reacted CuCl from the MS data treatment and height of the peak at 1.5eV from the KM-function vs. photoenergy plot in the UV-vis. Data corresponding to the second step of the experiment 14_3. **T** = 483K; **PO$_2$** = 0.223 atm.

The two following figures correspond to the fitting using the maximum value in the peak around 3.5eV. In this case the maximum point could not be known because of the noise so it's used the closest one possible instead.

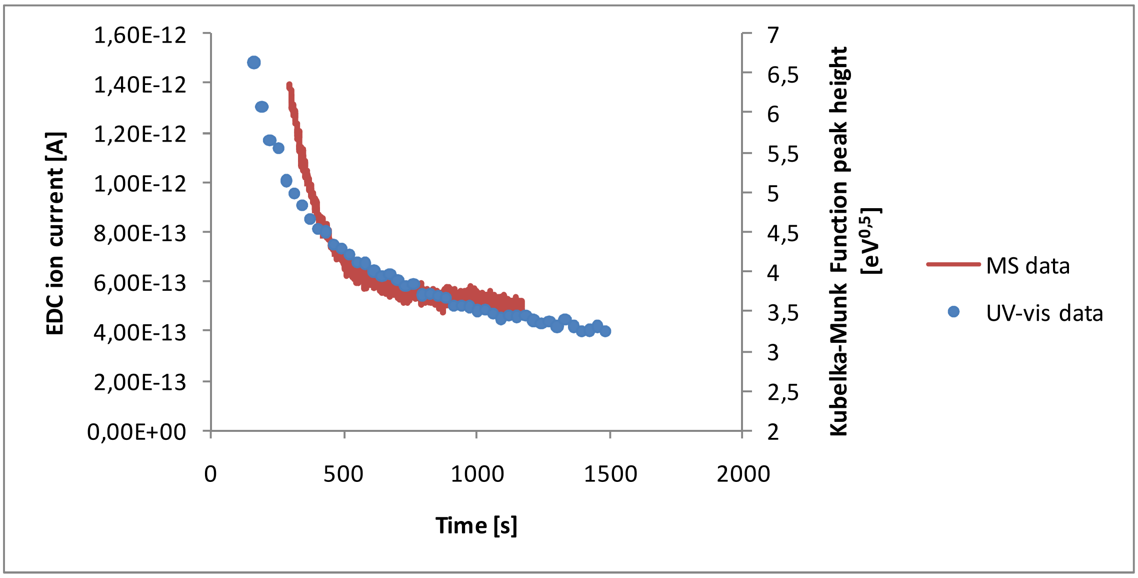


Figure 3.20 Intensity of the corresponding EDC ion in the MS and the closest value from the peak at 3.5eV from the KM-function vs. photoenergy plot in the UV-vis. Data corresponding to the first step of the experiment 14_3. **T** = 483K; **PC$_2$H$_4$** = 0.085 atm.

In this case the UV-vis data does not fit as well to the EDC profile as in the figure 3.18. The decrease of the peak value is not as drastic as the amount of EDC during the experiment.

On the other hand, the fitting for the second step is very accurate. The max peak point rises as fast as the amount of reacted CuCl and the curve shape is very similar. Among the three different fittings this one seems to be the best way to correlate the data for the second step. Of course the maximum peak value would be needed for a sharper fitting, but before that the noise in low wavelengths of the UV-vis spectra should be reduced.

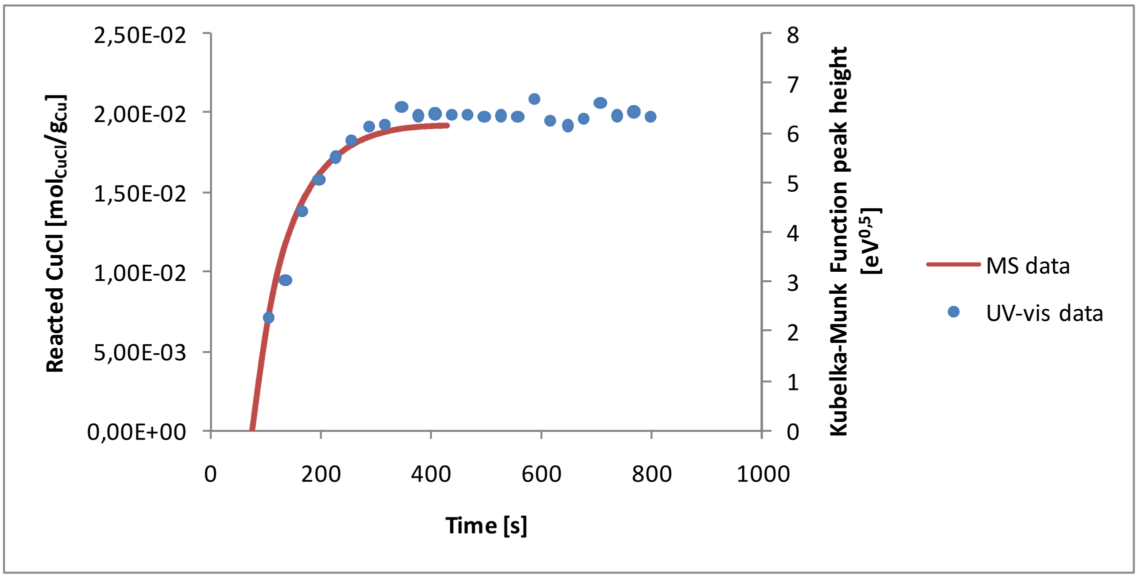


Figure 3.21 Calculated amount of reacted CuCl from the MS data treatment and the closest value from the peak at 3.5eV from the KM-function vs. photoenergy plot in the UV-vis. Data corresponding to the second step of the experiment 14_3. **T** = 483K; **PO$_2$** = 0.223 atm.

Finally one last fitting is done using the AEE. The process followed to process the data is explained in the section 2.3.3.

In this case the AEE evolution during the first step is more linear than in the other fittings done. The difference between the UV-vis data profile and the MS one is higher here and seems harder to correlate these two sets of data than the one where the peak height at **1.5eV** was used.

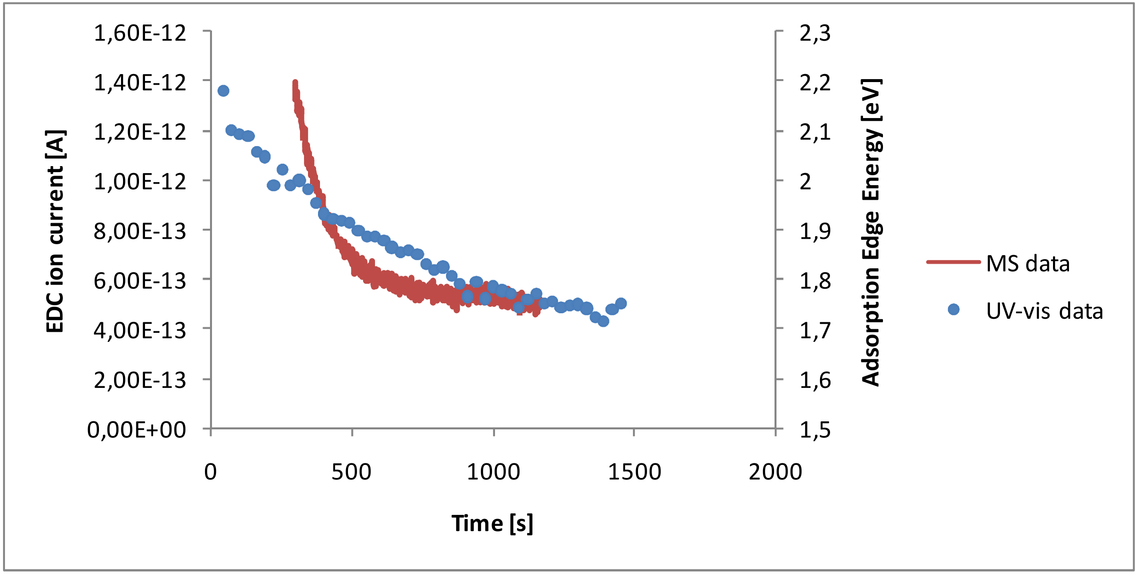


Figure 3.22 Intensity of the corresponding EDC ion in the MS and the AEE value in the UV-vis. Data corresponding to the first step of the experiment 14_3. **T** = 483K; **PC$_2$H$_4$** = 0.085 atm.

There's also a difference in the AEE scale between the figures 3.22 and 3.23, this might be for the same reason as in the fitting at **1.5eV**, but it's not so clear yet why there are these small changes in the UV-vis spectra when there's no reactant flowing.
The fitting for the second step is better than for the first step, but still not as good as the one in the figure 3.21.

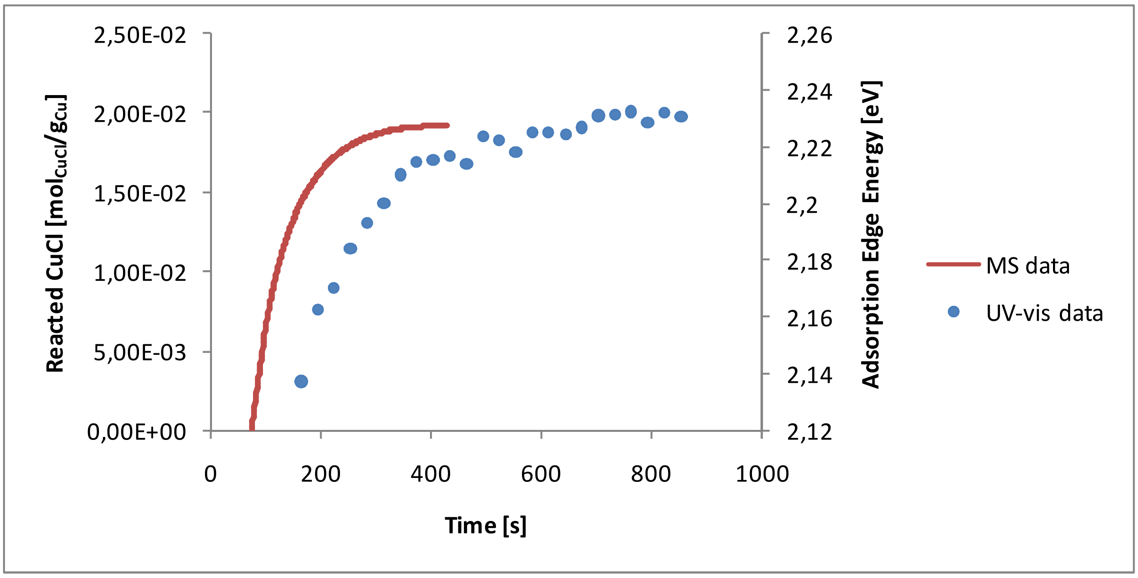


Figure 3.23 Calculated amount of reacted CuCl from the MS data treatment and the AEE value in the UV-vis. Data corresponding to the second step of the experiment 14_3. **T** = 483K; **PO$_2$** = 0.223 atm.

In all three cases it was seen that there's a relation between the UV-vis and MS data in some cases much closer than others. For the first step the peak height around **1.5eV** gave good results, the only thing needed is a better correction in the calculations, which are not easy to solve. Once the peak height can be get rid of the noise after the **500s** the fitting would be much closer and a correlation between the data could be established.

The best fitting achieved for the second step is the one where the maximum value available from the peak at **3.5eV** was used. For this case a way to reduce the noise in low wavelengths is needed in order to use the highest value which now is covered by all the noise.

3.8. uptake

In the tables 3.7 and 3.8 the results from the table 3.2 are displayed in a way where their dependence on the pressure and the temperature can be compared.
All the sets of experiments are done with constant temperature and changing the partial pressure of ethylene or oxygen in the corresponding step. This means that the comparison between different temperatures is always a comparison between different sets of experiments.
For the partial pressure is just the opposite, the experiments at different partial pressure and same temperature are done during the same set of experiments. In this case, the results have to be read carefully because the changes in different partial pressures results might be also due to the deactivation and not only to the experiment conditions.

In the next two tables there are some results in red color. This means that from the same result it can be deduced that the catalyst was not yet fully activated. If these results are compared with the results at the same temperature but different partial pressures this difference can be distinguished.

First of all the results from the first step are evaluated. At lower temperatures, the chlorine uptake has low changes depending on the partial pressure; these changes are probably because of the experimental error so the direct influence of the partial pressure on the chlorine uptake seems to be rather small. At higher temperatures there's a clear difference in the results, but it not so clear that this is the influence of the pressure. As said before the experiments at different partial pressures were run in the same set (having one or two sets per each temperature) so it's likely that the decrease of the chlorine uptake is due to the catalyst deactivation.

Table 3.7 Chlorine uptake (mol_{Cl}/g_{Cu}) for each experimental condition in the first step.

T (K)	PC_2H_4 (atm)	0,0579	0,0647	0,0733	0,0846	0,100
	483	0,00739	0,00795	0,00775	0,00723	0,00765
	493	0,00594	0,00760	0,00760	0,00731	-
	508	0,00963	0,01071	0,01065	0,00882	-
	523	-	0,01008	0,00941	0,00929	0,00814

The temperature effect on the chlorine uptake is clearer than the pressure. The total uptake rises as the temperature is increased, but there's a big difference between the experiments at **493K** and **508K**. Some more experiments should be done in between to ensure that the uptake depends directly on the temperature.

During the second step the temperature influence is not that clear. Logically the CuCl reacted should increase at higher temperatures because, as just discussed the results of the first step, the chlorine uptake also rises at higher temperatures and, therefore, more copper is reduced during the first step and more copper should be oxidized during the second one. In some cases, the reacted CuCl increases with the temperature but in other cases, as in the experiments at **0.301 atm**, it's just the opposite.

The pressure comparison is also troublesome as in the table 3.7 because of the same reasons. There is some drop in the reacted CuCl as the pressure increases but that's not clear if this is caused by the deactivation of the catalyst during the experiments or because that is how the pressure really affects the reaction. It is easier to think about the deactivation because normally the higher the partial pressure is, the bigger the conversion is in a reaction; here is just the way around and that's why the deactivation is heavily considered.

Table 3.8 CuCl reacted (mol_{CuCl}/g_{Cu}) for each experimental condition in the second step.

PO₂ (atm) **T (K)**	**0,147**	**0,177**	**0,223**	**0,301**	**0,365**	**0,463**
483	0,01072	0,01318	0,0192	0,01901	0,01086	0,00956
493	-	-	0,02709	0,01352	-	0,00948
508	-	-	0,02064	0,01133	-	0,01023
523	0,01164	0,01166	0,01097	0,01002	-	-

In order to make a better comparison some sets of experiments should be run at the same partial pressure and changing the temperature on every cycle. This way the different partial pressures at different temperatures could be compared because they would be run also in the same cycle of their corresponding set of experiments.

3.9. Kinetic model

At this point a model needs to be proposed for the first and second step. One reaction mechanism is set for each step and then the reaction rate equations are deduced for each step in each mechanism. Since it's almost impossible to calculate the rates for every step, the equation corresponding to the rate determining step is the one used for the fitting.

The following equations show the mechanism for the ethylene chlorination step which consists of the adsorption, first chlorination, second chlorination and desorption.

$$C_2H_4 + * \rightleftarrows^{k_{I1}}_{k_{-I1}} C_2H_4 * \qquad [3.1]$$

$$C_2H_4 * + Cl \rightleftarrows^{k_{I2}}_{k_{-I2}} C_2H_4Cl * \qquad [3.2]$$

$$C_2H_4Cl * + Cl \rightleftarrows^{k_{I3}}_{k_{-I3}} C_2H_4Cl_2 * \qquad [3.3]$$

$$C_2H_4Cl_2 * \rightleftarrows^{k_{I4}}_{k_{-I4}} C_2H_4Cl_2 + * \qquad [3.4]$$

For the equations [3.2], [3.3] and [3.4] the rate equation is calculated under the hypothesis of being the rate determining step:

$$r = \frac{k_{I2}K_{I1}c_TP_{C_2H_4}C_{Cl}}{1 + K_{I1}P_{C_2H_4}} \qquad [3.5]$$

$$r = \frac{k_{I3}K_{I1}K_{I2}C_TP_{C_2H_4}C_{Cl}^2}{1 + K_{I1}P_{C_2H_4} + K_{I1}K_{I2}P_{C_2H_4}C_{Cl}} \qquad [3.6]$$

$$r = \frac{k_{I4}K_{I1}K_{I2}K_{I3}C_TP_{C_2H_4}C_{Cl}^2}{1 + K_{I1}P_{C_2H_4} + K_{I1}K_{I2}P_{C_2H_4}C_{Cl} + K_{I1}K_{I2}K_{I3}P_{C_2H_4}C_{Cl}^2} \qquad [3.7]$$

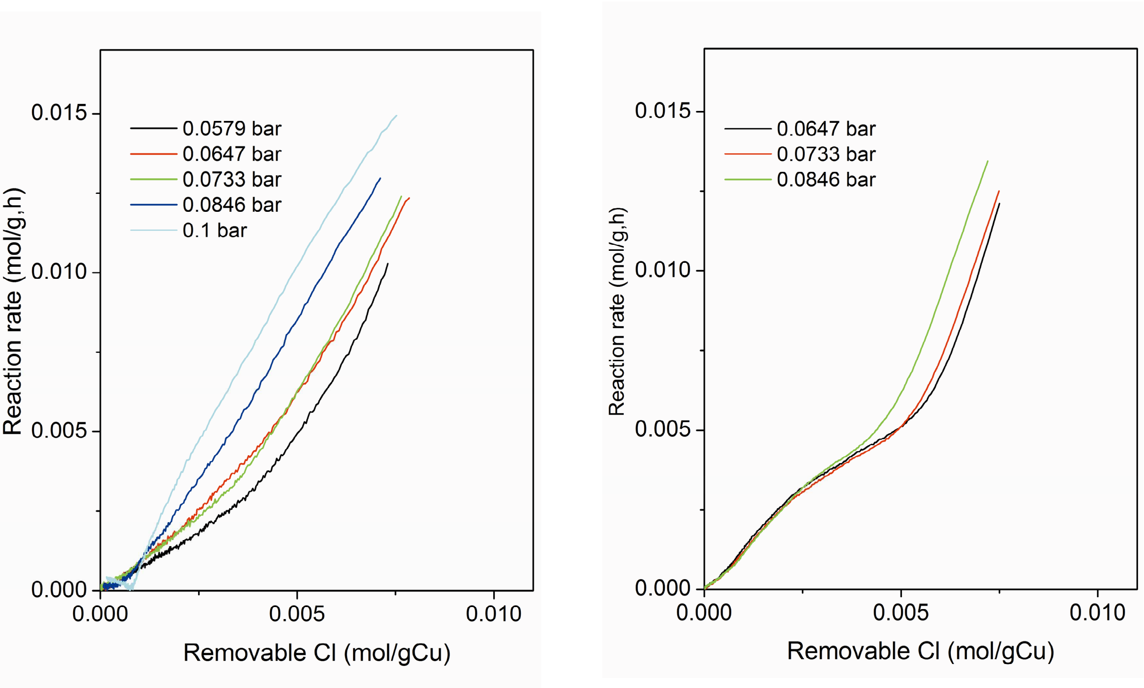
From these three steps the one that is more likely to be the rate determining step is the second chlorination. This decision is based in the principle that the second chlorination is harder because only one of the two carbons from the EMC is ready to react while in the first chlorination both carbons can be chlorinated.

Then the equation [3.6] is the used for the kinetic fitting, but before it can be simplified by making the hypothesis that the ethylene adsorption will happen relatively much faster than the chlorination: $K_{I1} \cdot P_{C2H4} \approx 0$.

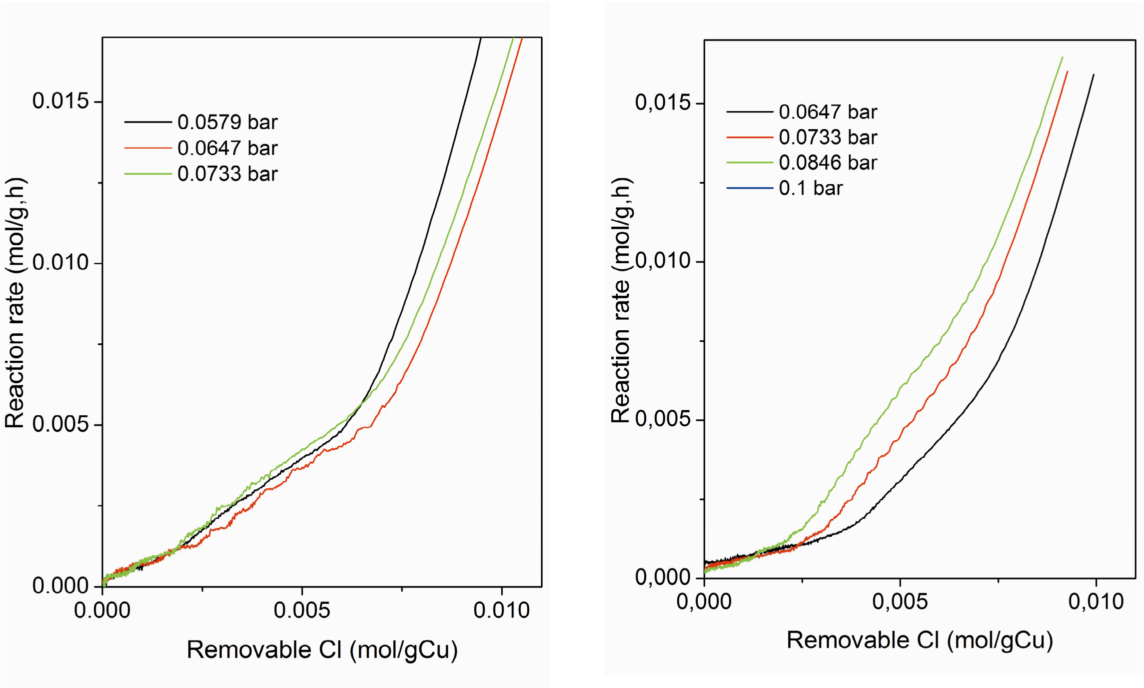
$$r = \frac{k_I K_I P_{C_2H_4} C_{Cl}^2}{1 + K_I P_{C_2H_4} C_{Cl}} \qquad [3.8]$$

The following figures show the reaction rate of each experiment plotted versus the available chlorine on the catalyst. In almost all the lines there’s a clear dependence between the partial pressure of ethylene and the reaction rate, the experiments which were performed at higher partial pressures show higher rate profiles.

The data is gathered depending on the conditions of the experiments, in every figure the experiments done at the same temperature are plotted together and there’s one figure for each temperature.



Figures 3.24 and 3.25 Reaction rate plotted versus the available chlorine in the catalyst during the experiment. (left) **T** = 483K; **w_{Cu}** = 6.11%. (right) **T** = 493K; **w_{Cu}** = 6.11%.



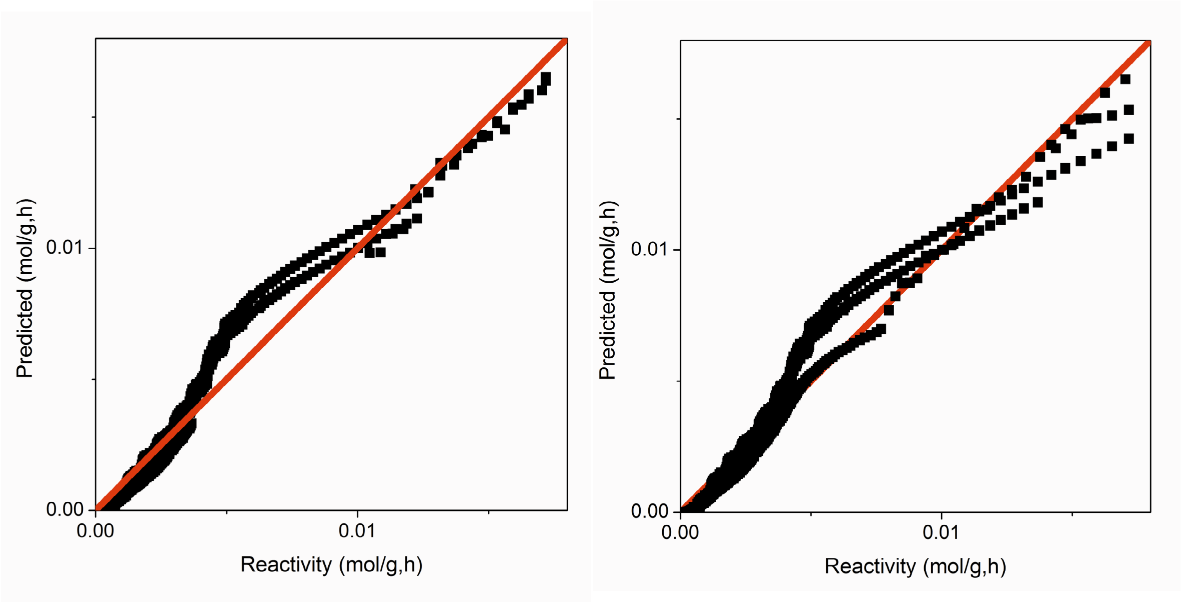
Figures 3.26 and 3.27 Reaction rate plotted versus the available chlorine in the catalyst during the experiment. (left) **T** = 508K; $\mathbf{w_{Cu}}$ = 5.77%. (right) **T** = 523K; $\mathbf{w_{Cu}}$ = 5.77%.

The fitting is done at three different temperatures: **483K**, **493K**, **508K** and **523K**. In the table 3.9 these parameters are gathered. Comparing the different data depending on which step is supposed to be the rate determining one we confirm that the second chlorination is the slowest one with the lower kinetic constant.

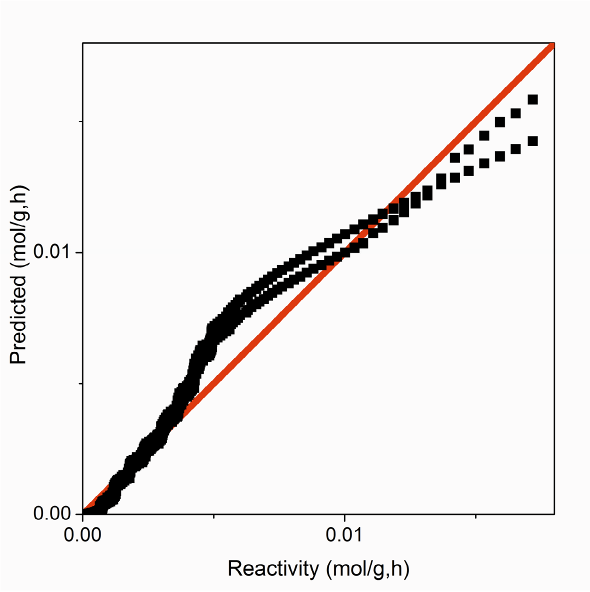
Table 3.9 Parameters from the fitting at different temperatures for the first step.

T (K)	RDS	k_{I2}	k_{I3}	k_{I4}	K_{I1}	K_{I2}	K_{I3}	R^2
	I2	16.1			-1.39			0.961
483	I3		2.87			2660		0.962
	I4			5850			249000	0.970
	I2	34.6			13.86			0.966
493	I3		1.33			55100		0.963
	I4			6740			471000	0.944
	I2	-40.7			-59.2			0.870
508	I3		2.59			1400		0.936
	I4			2430			34000	0.937
	I2	12.8			-0.406			0.885
523	I3		3.16			1090		0.968
	I4			2800			72133	0.969

Three more plots are done comparing the results obtained from the experiments and from the predicted data in the model proposed. The model show that the rate value goes higher than it should be at some point. Taking into account the difficulty of getting good results in this kind of study the rate prediction is close enough at some parts and it could be improved to minimize the difference.



Figures 3.28 and 3.29 Predicted reaction rate plotted versus the reaction rate obtained in the first reaction step experiments. (left) **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11%. (right) **T** = 508K; $\mathbf{w_{Cu}}$ = 5.77%.



Figures 3.30 Predicted reaction rate plotted versus the reaction rate obtained in the first reaction step experiments. **T** = 523K; $\mathbf{w_{Cu}}$ = 5.77%.

For the second step the same procedure is followed. The mechanism in this case is easier than the mechanism proposed for the first step. As before, the rate determining step here is the reaction [3.10].

$$\frac{1}{2}O_2 + * \underset{k_{-II1}}{\overset{k_{II1}}{\rightleftarrows}} O* \qquad [3.9]$$

$$2CuCl + O* \underset{k_{-II2}}{\overset{k_{II2}}{\rightleftarrows}} Cu_2OCl_2* \qquad [3.10]$$

$$Cu_2OCl_2* \underset{k_{-II3}}{\overset{k_{II3}}{\rightleftarrows}} Cu_2OCl_2 + * \qquad [3.11]$$

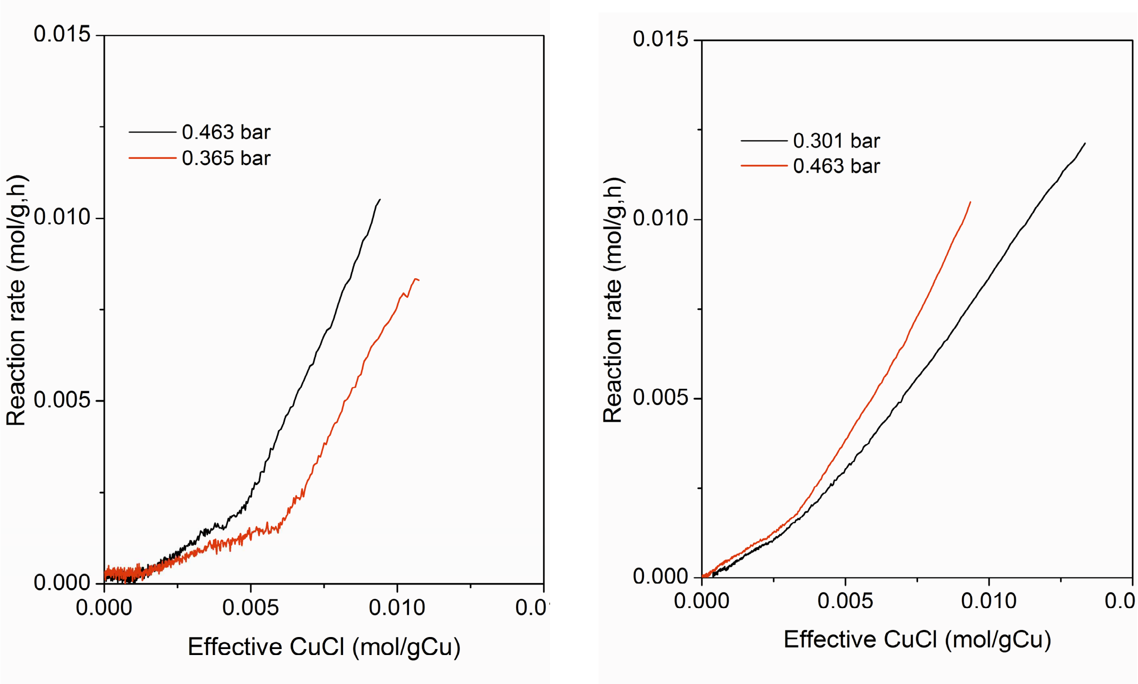
The rate equation for the steps [3.10] and [3.11] is then deduced and displayed as follows:

$$r = \frac{k_{II2}K_{II1}C_T C_{CuCl}^2 P_{O_2}^{0.5}}{1 + K_{II1}P_{O_2}^{0.5}} \qquad [3.12]$$

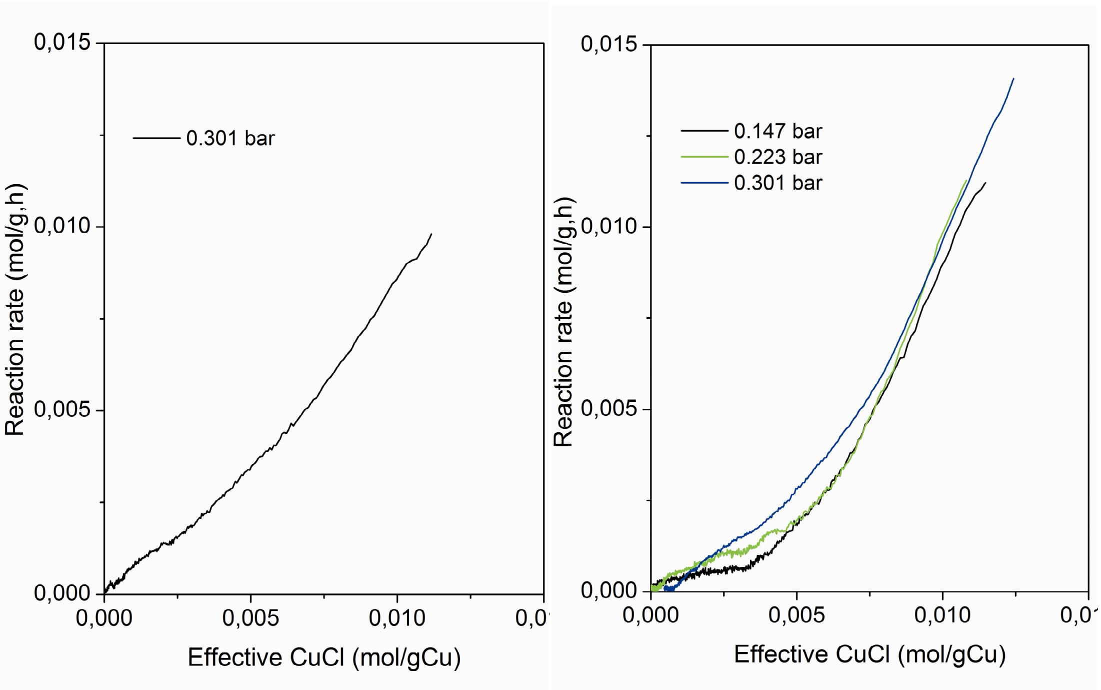
$$r = \frac{k_{II3}K_{II1}K_{II2}C_T C_{CuCl}^2 P_{O_2}^{0.5}}{1 + K_{II1}P_{O_2}^{0.5} + K_{II1}K_{II2}C_{CuCl}^2 P_{O_2}^{0.5}} \qquad [3.13]$$

As said before, the reaction step is decided to be the rate determining step so the equation [3.12] is the one to be used.

The data from which the fitting is done is fewer for the second step. The reason is that sometimes higher partial pressures of oxygen were used and that caused a bad blank recording and the uselessness of the data of these experiments.



Figures 3.31 and 3.32 Reaction rate plotted versus the available CuCl in the catalyst during the experiment. (left) **T** = 483K; $\mathbf{w_{Cu}}$ = 6.11%. (right) **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11%.



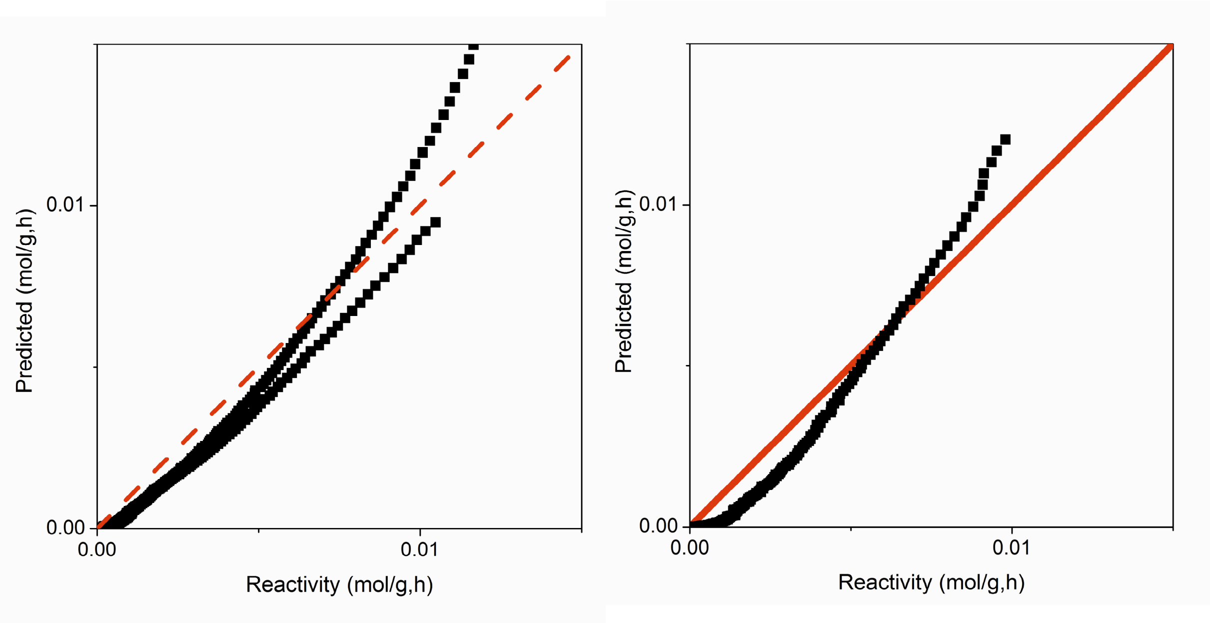
Figures 3.33 and 3.34 Reaction rate plotted versus the available CuCl in the catalyst during the experiment. (left) **T** = 508K; $\mathbf{w_{Cu}}$ = 5.77%. (right) **T** = 523K; $\mathbf{w_{Cu}}$ = 5.77%.

In the table 3.10 the results from the fitting for this second step are gathered.

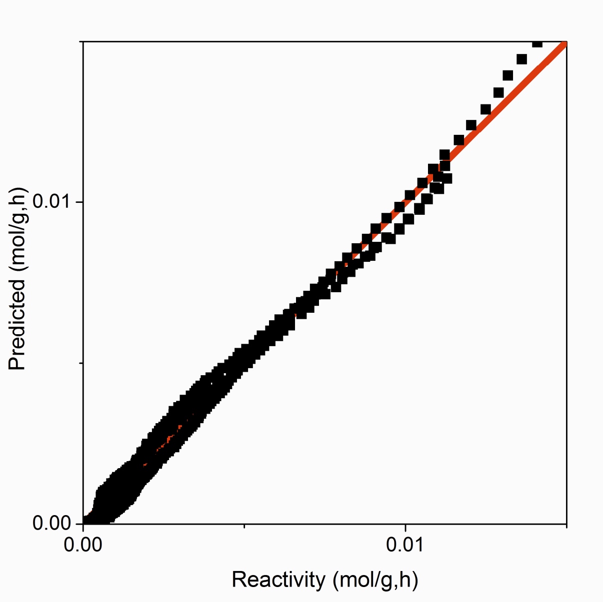
Table 3.10 Parameters from the fitting at different temperatures for the second step.

T (K)	RDS	k_{I2}	k_{I3}	K_{I1}	K_{I2}	R^2
493	I2	175		0.15		0.96
	I3		167	0.05	22.1	0.85
508	I2	364		1.97		0.95
	I3		0.4	228	239	0.93
523	I2	520		3.55		0.98
	I3		0.5	3.26	311	0.98

Finally the model is checked comparing the predicted results with the experimental ones. The next figures show that in his case fitting is much better than in the first step. The predicted values go really close to the experimental ones and in some cases at high rates the error increases.



Figures 3.35 and 3.36 Predicted reaction rate plotted versus the reaction rate obtained in the second reaction step experiments. (left) **T** = 493K; **w**$_{\mathbf{Cu}}$ = 6.11%. (right) **T** = 508K; **w**$_{\mathbf{Cu}}$ = 5.77%.



Figures 3.37 Predicted reaction rate plotted versus the reaction rate obtained in the second reaction step experiments. **T** = 523K; **w**$_{\mathbf{Cu}}$ = 5.77%.

4. Future plans and ideas

After all the experiments, results and discussion, there are some areas of study that could be extended or improved in order to go further in the research.

From the study of the catalyst activation it was considered that one reason that caused the low conversions during the first cycle is the lower amount of chlorine in the fresh catalyst. This could be related to the adsorption of the HCl to the support. The idea here is to start the first cycle from a set of experiments with the third step (catalyst chlorination) and compare the results of the next ethylene chlorination with the previous results. It’s expected that with the only HCl step before the first ethylene chlorination the conversion should be similar to the results in the second cycle of the previous experiments.

Since the kinetic model has just been tested for individual step experiments, combined step experiments should be done. Then the model can be compared and corrected with the integration of multiple steps in the same experiment, as running experiments with all three reactants at the same time.

The deactivation has been studied only for two different temperatures and it would provide more information about the deactivation the study of it at some more temperatures. This way we can know from which temperature the deactivation starts to be significant.

In the UV-vis spectra there was noise present in wavelengths lower than 400nm. This noise appeared right after the light bulb was changed, where the noise started at a wavelength of 200nm. There is important information in the range of 200nm – 400nm like the maximum peak value around 3.5eV which cannot be known right now because of this problem. Therefore this should be solved as soon as possible for a better UV-vis data recording.

When the experiments are done, the temperature is kept during the set and only the partial pressure is changed. Some experiments should be done the way around, keeping the partial pressure during the set of experiments and changing the temperature. By doing this it will be easier to distinguish whether the results differences are because of the different conditions of temperature and pressure used or because of the catalyst deactivation in later cycles.

5. Conclusions

When it comes to start a set of experiments the moment where the catalyst is fully activated is not controlled yet. Sometimes in the second cycle the results show that the catalyst is fully activated, but in some other cases this does not happen before the third cycle.

After studying the deactivation it could be related that higher temperatures bring the catalyst to lose activity faster. The amount of reduced $CuCl_2$ showed clearer results regarding the deactivation and the partial pressure had no influence in the catalyst deactivation since experiments at the same temperature and different partial pressure showed the same deactivation rate and only different absolute values of chlorine uptake.

The deactivation of the catalyst also depended on the reaction step. The second and third steps were thought to be responsible of the deactivation in a high measure. The deactivation during the catalyst rechlorinaton was higher than the deactivation during the oxidation.

Another measuring method as the pH-meter usage was proposed to record the amount of HCl in the reactor outlet stream because it was adsorbing on the MS capillary lines and the data recorded in the MS during that step was useless. The adsorption to the support is also something which might cause problems; it has to be ensured that the HCl adsorption amount per support mass keeps constant whether there’s only support or it’s with the catalyst.

For the synchronization between the MS and UV-vis data there was a relation between the surface change and the concentration of reacted chlorine or CuCl. Even though this still needs a huge development it was observed that there was the possibility to go further and the first requirement is to reduce the noise from the UV-vis data.

The kinetic model showed good results but is still far from a good enough model. This was a first approximation, but it’s being improved in order to get sharper predicted results from the experimental data fittings.

6. Nomenclature

Table 6.1 Nomenclature used in the equations

Symbol	Magnitude	Units
W	Mass fraction	w/w
m	Mass	g
M	Molar mass	g/mol
PV	Pore volume	$g_{H2O}/g_{support}$
H_i	Hydration ratio	mol_{H2O}/mol_i
$\vec{F}$	Force	N
q	Electric charge	C
$\vec{E}$	Electric field	N/C
$\vec{v}$	Lineal velocity	m/s
$\vec{B}$	Magnetic field	T
$\vec{a}$	Acceleration	m/s^2
$\dot{V}$	Volumetric flow	ml/s
X	Conversion	mol/mol
$\dot{n}$	Molar flow	mol/s
AP	MFC aperture	%
t	Time	s
k	Kinetic constant	(depends on the equation)
R	Ideal gas constant	J/(mol·K)
P	Pressure	atm
T	Temperature	K
ratio	Molar ratio	mol
c	Light velocity	m/s
h	Planck’s constant	eV·s/cycle
λ	Wavelength	nm
R_∞	Reflectance	%
hν	Photon energy	eV
r	Reaction rate	$mol/(g_{cat}\cdot s)$
IU	Intregral uptake of Cl^- or CuCl	mol/g_{Cu}
$F(R_\infty)$	Kubelka-Munk Function	Non-dimensional
I	Intensity	A

Table 6.2 Subscripts used in the equations

Subscripts	meaning
Cu	Copper $^{2+}$
$CuCl_2$	Copper chloride
$CuCl_2 \cdot 2H_2O$	Dehydrated copper chloride
C_2H_4	Ethylene
$C_2H_4Cl_2$	Ethylene dichloride
cat	Catalyst
sup	Support
impregnated	Impregnated in the catalyst
t	Theoretical
ss	Steady State
r	Real/measured
max	Maximum value from the set of data
min	Minimum value from the set of data
reactant	Corresponding reactant: C_2H_4, O_2 or HCl
inert	Corresponding inert gas: Ar or He
blank	Blank data
air	Air
O_2	Oxygen
He pure	He used in the inert-only stream
Ar pure	Ar used in the inert-only stream
He	He used for diluting the reactant concentration
Ar	Ar used for diluting the reactant concentration
HCl	Hydrochloric acid

7. Bibliography

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APPENDIX

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Appendix A: UV-vis data

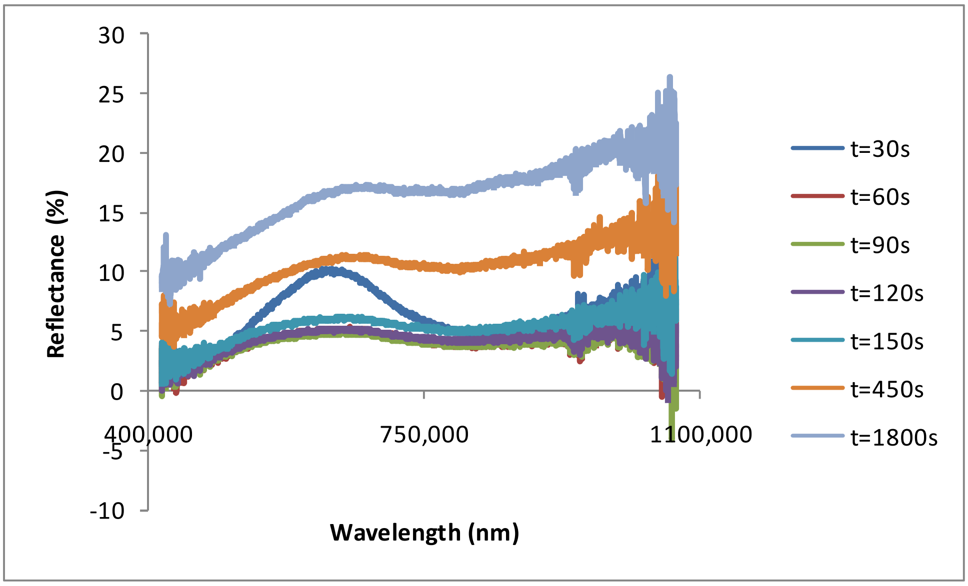

Figure A.1 UV-vis spectra evolution during the first reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

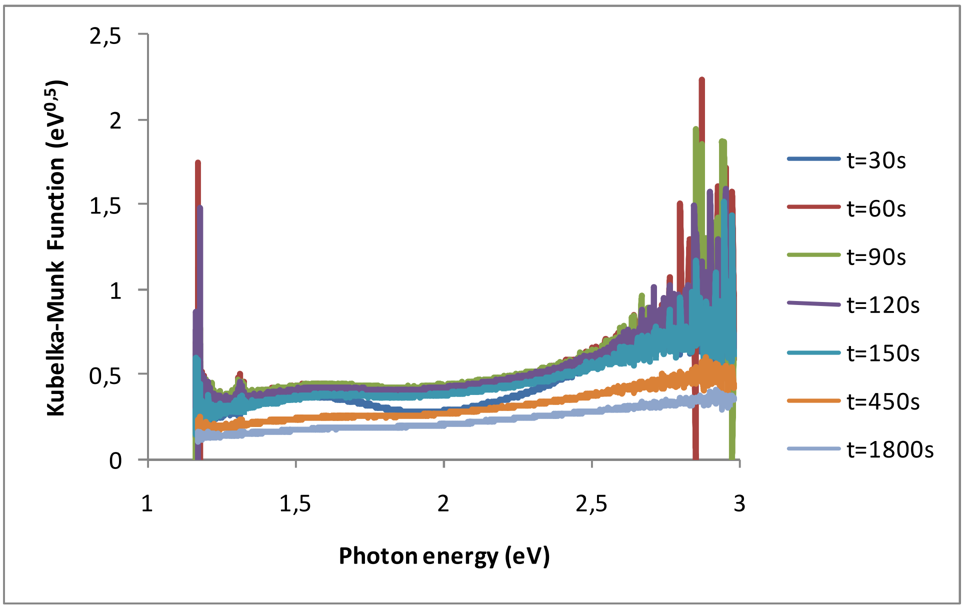

Figure A.2 UV-vis processed data evolution during the first reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

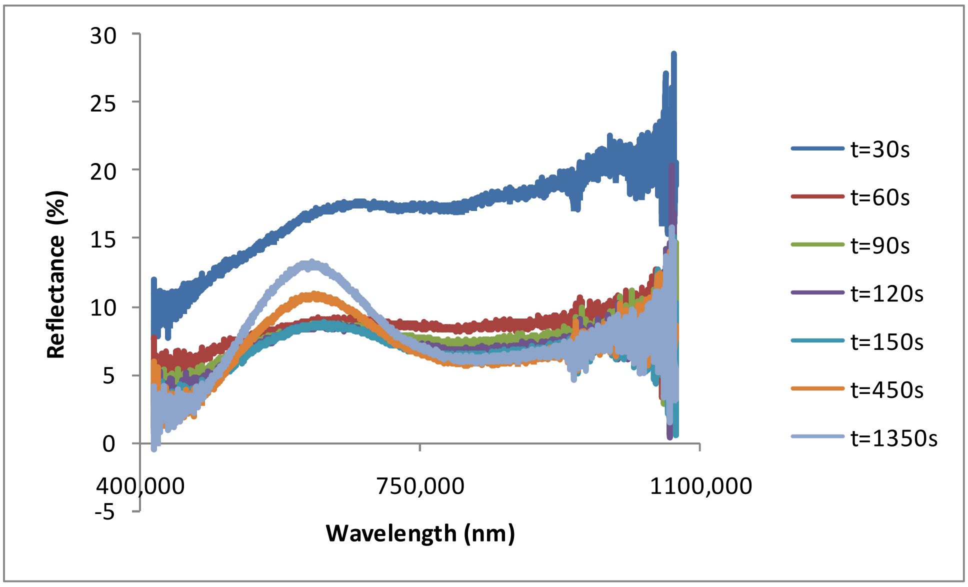

Figure A.3 UV-vis spectra evolution during the second reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.04 ml/s; $\mathbf{PO_2}$ = 0.223 atm; **T** = 483K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.523 g_{cat}.

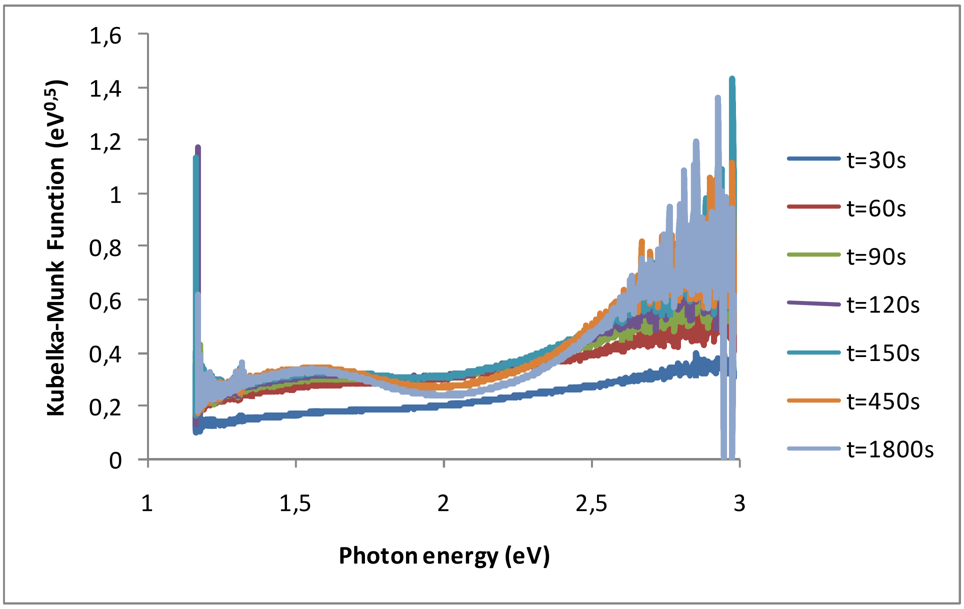

Figure A.4 UV-vis processed data evolution during the second reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.04 ml/s; $\mathbf{PO_2}$ = 0.223 atm; **T** = 483K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.523 g_{cat}.

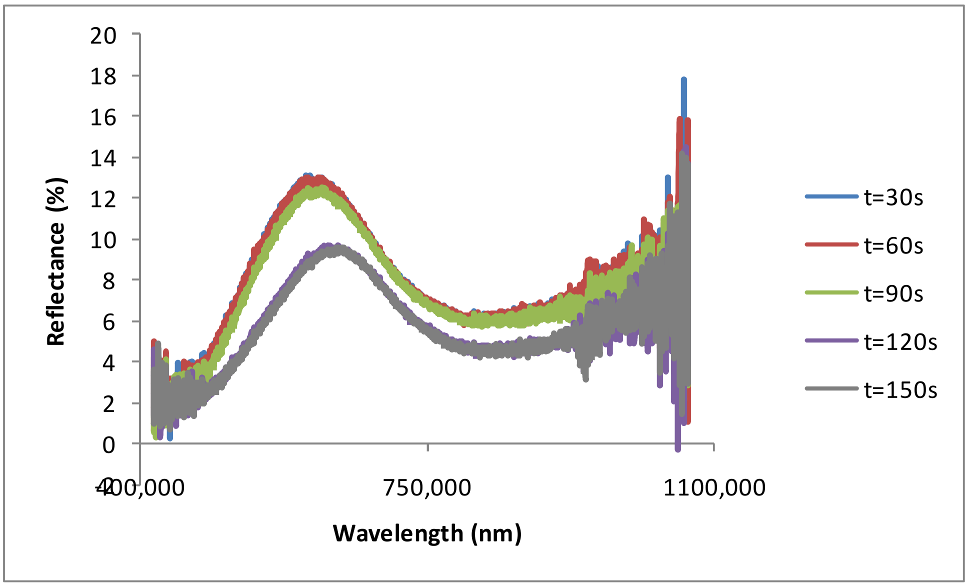

Figure A.5 UV-vis spectra evolution during the third reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.36 ml/s; **PHCl** = 0.05 atm; **T** = 483K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.523 g_{cat}.

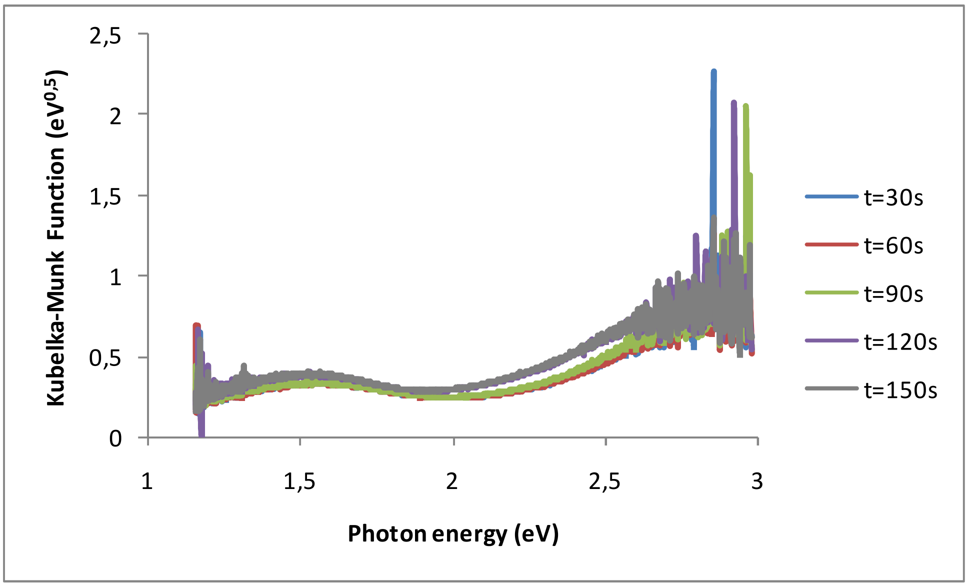

Figure A.6 UV-vis processed data evolution during the third reaction step of the experiment 14_3. Experimental conditions **Total flow** = 1.36 ml/s; **PHCl** = 0.05 atm; **T** = 483K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.523 g_{cat}.

Appendix B: XRD data

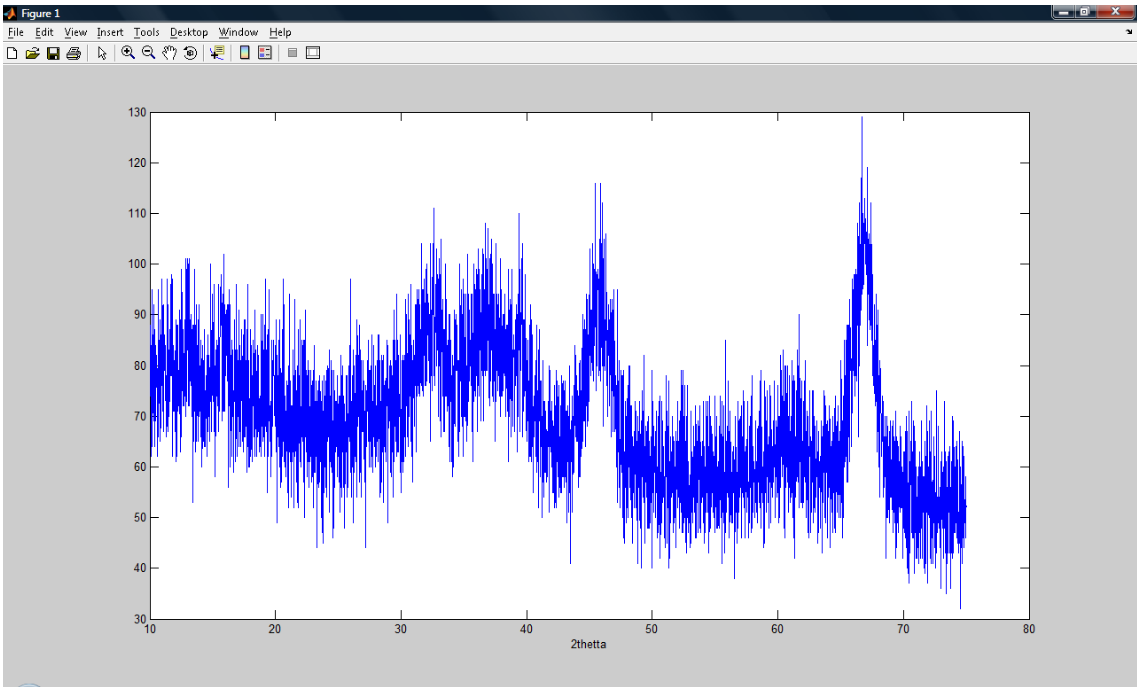

Figure B.1 XRD spectra of the catalyst used in the experiments 7_x. The last cycle performed with this catalyst was the ethylene chlorination.

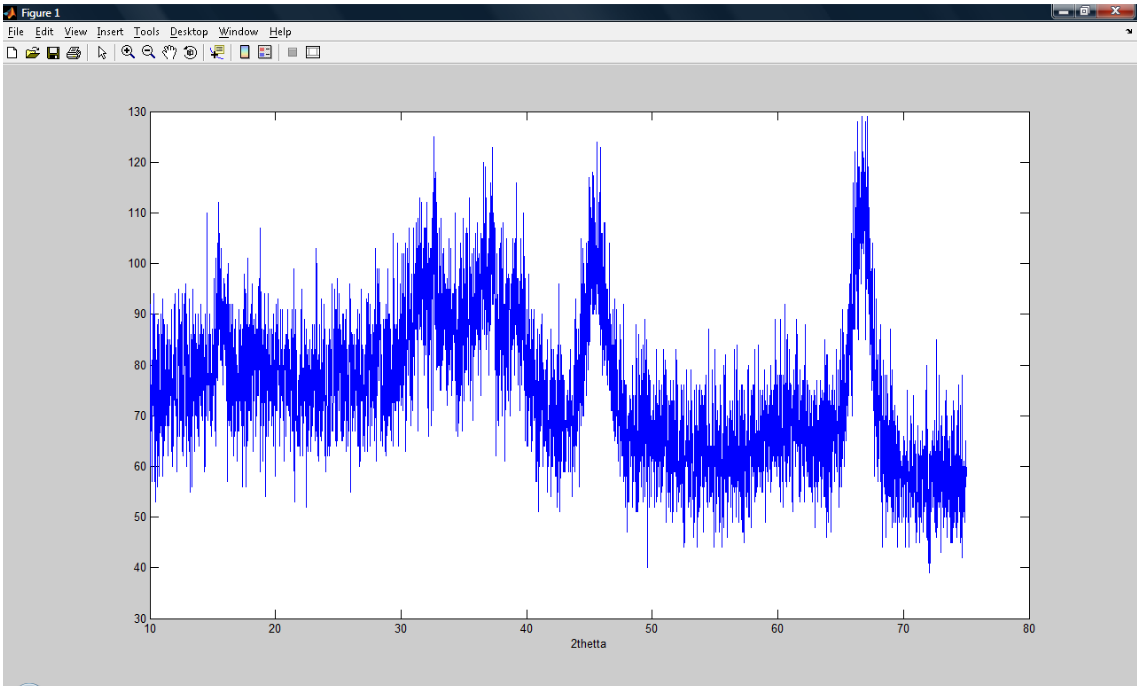

Figure B.2 XRD spectra of the catalyst used in the experiments 12_x. The last cycle performed with this catalyst was the ethylene chlorination.

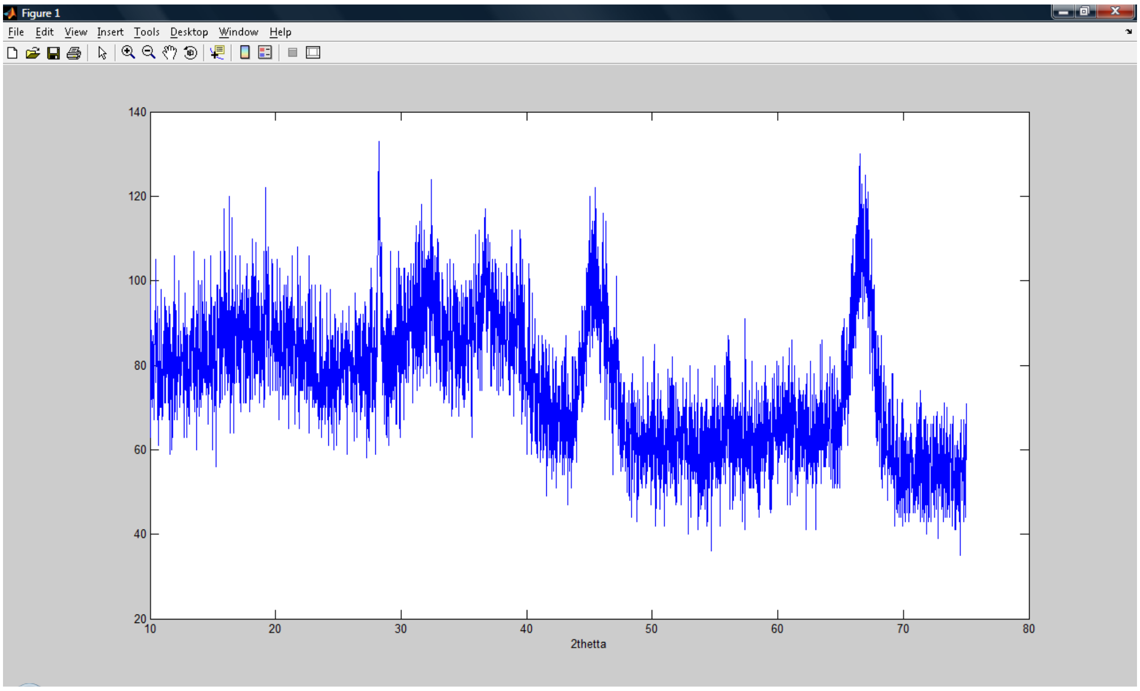

Figure B.3 XRD spectra of the catalyst used in the experiments 14_x. The last cycle performed with this catalyst was the ethylene chlorination.

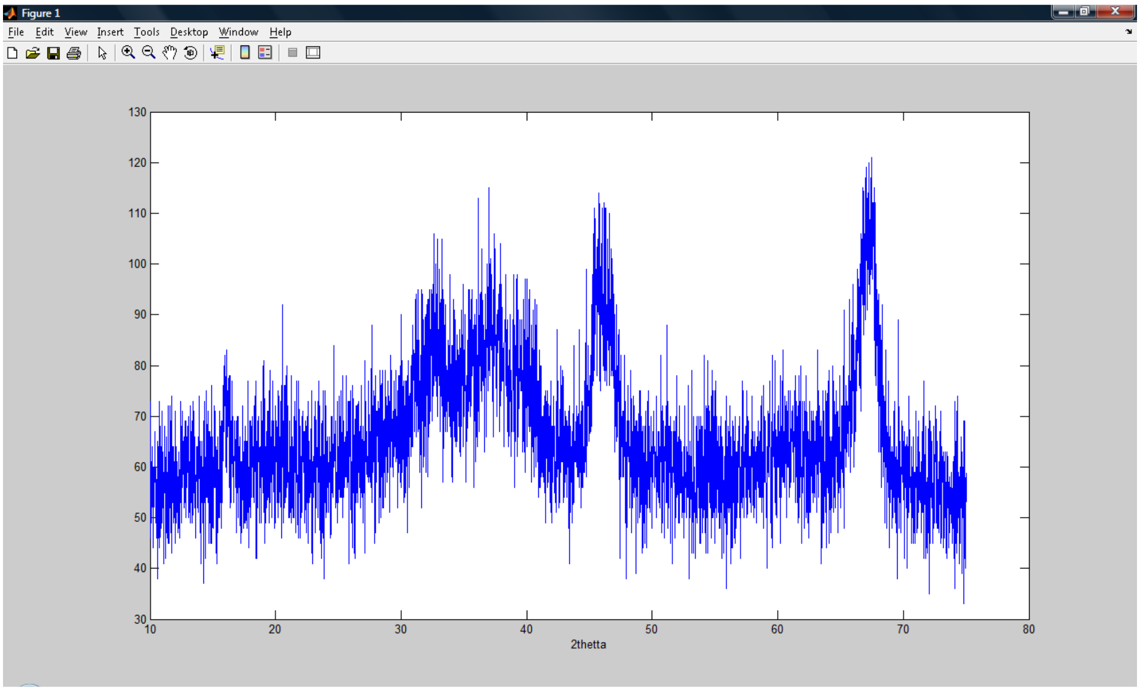

Figure B.4 XRD spectra of the catalyst used in the experiments 8_x. The last cycle performed with this catalyst was the oxidation.

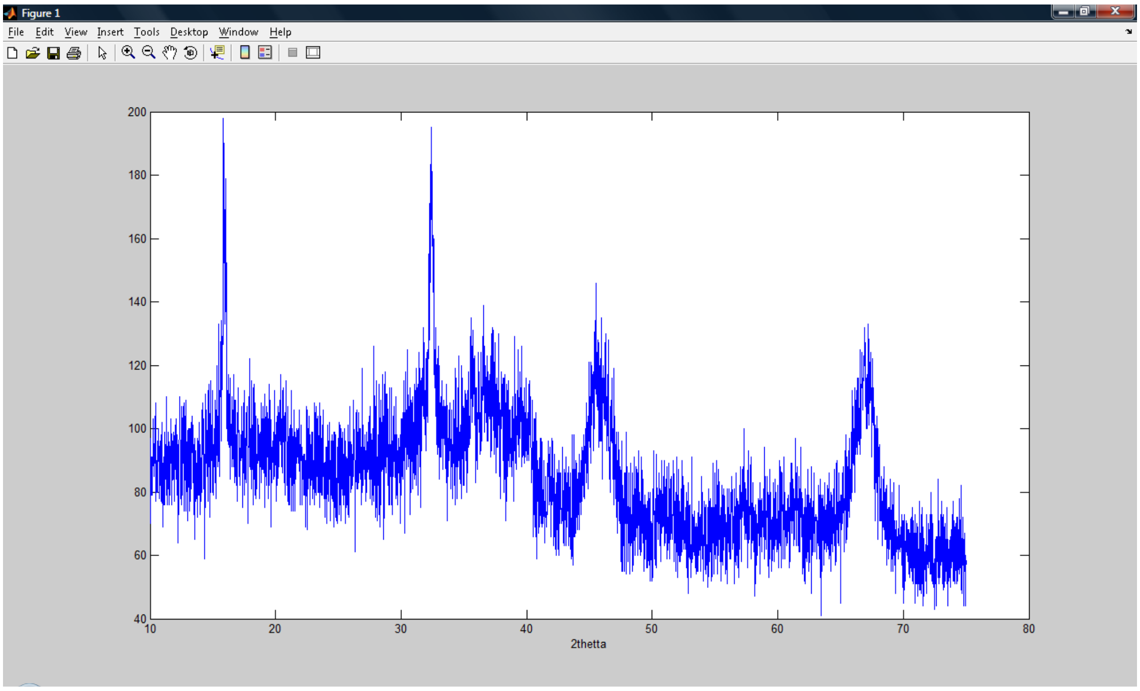

Figure B.5 XRD spectra of the catalyst used in the experiments 9_x. The last cycle performed with this catalyst was the oxidation.

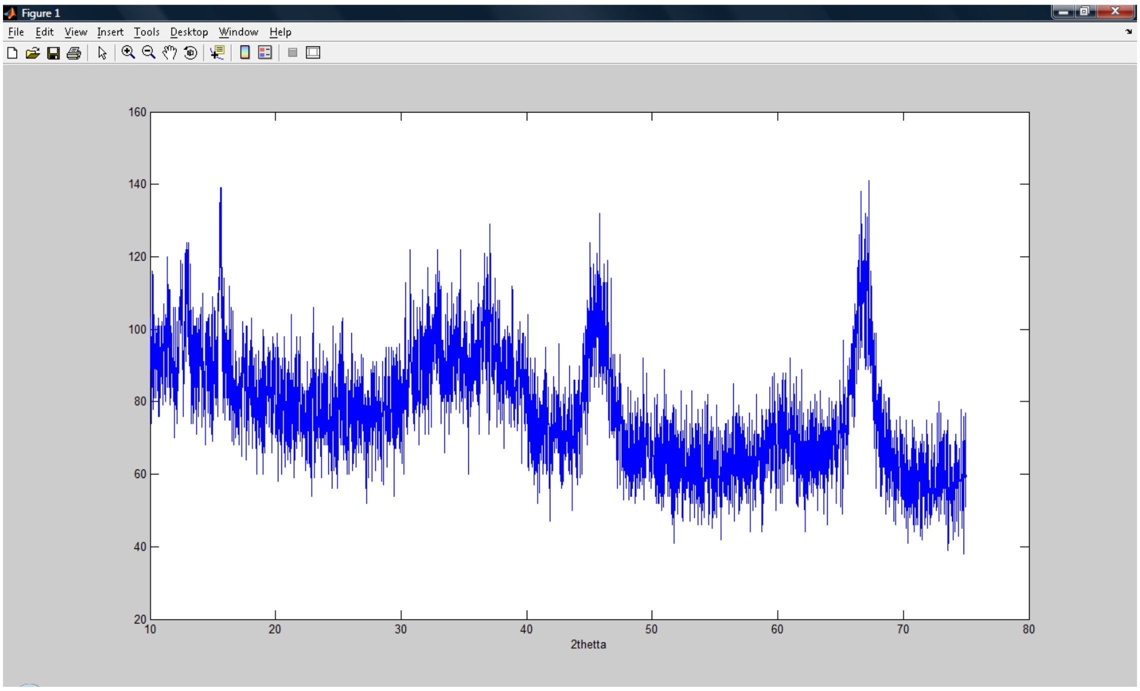

Figure B.6 XRD spectra of the catalyst used in the experiments 13_x. The last cycle performed with this catalyst was the oxidation.

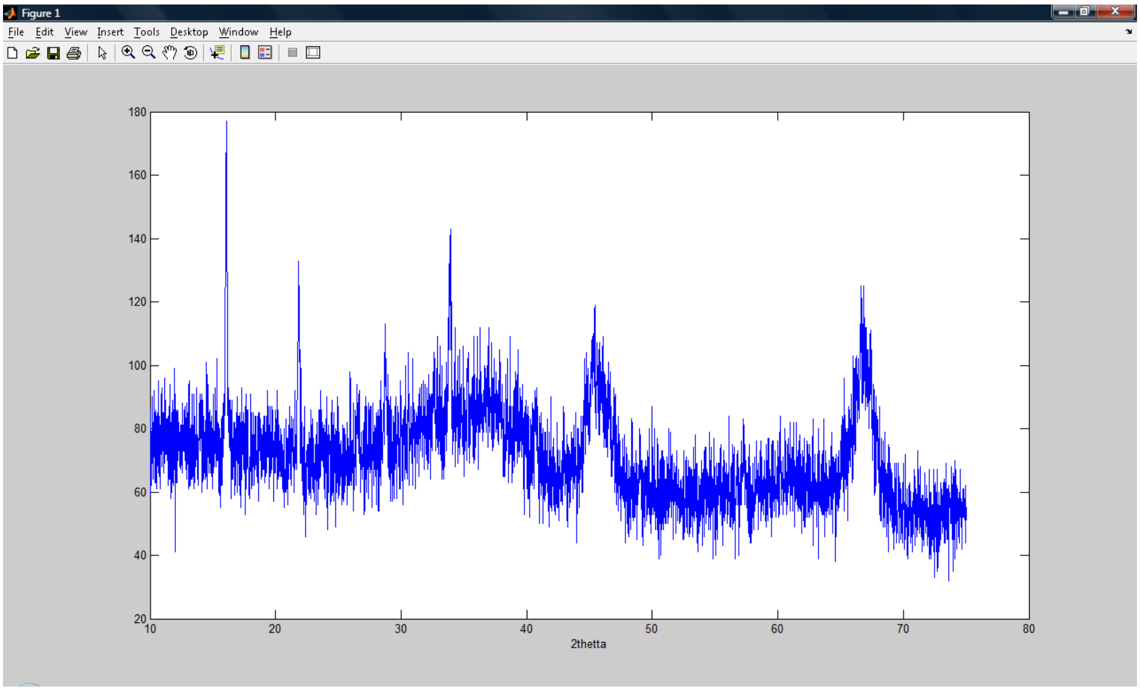

Figure B.7 XRD spectra of the catalyst used in the experiments 5_x. The last cycle performed with this catalyst was the catalyst rechlorination.

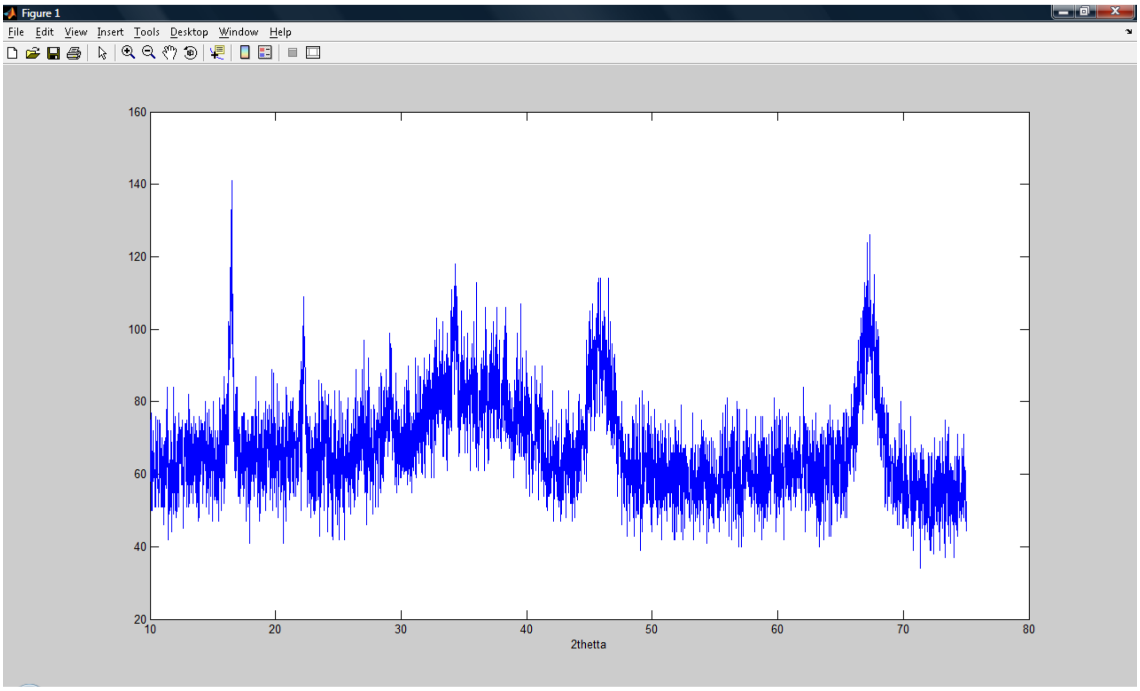

Figure B.8 XRD spectra of the catalyst used in the experiments 10_x. The last cycle performed with this catalyst was the catalyst rechlorination.

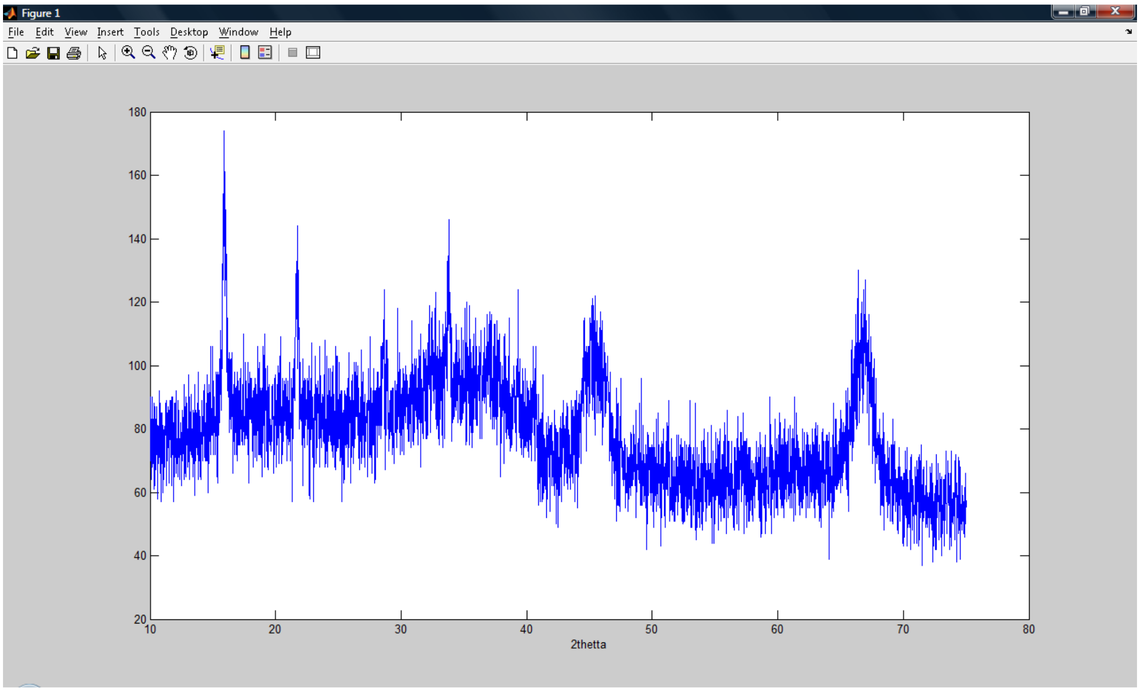

Figure B.9 XRD spectra of the catalyst used in the experiments 11_x. The last cycle performed with this catalyst was the catalyst rechlorination.

Appendix C: MS data

Experiment 6_1 data

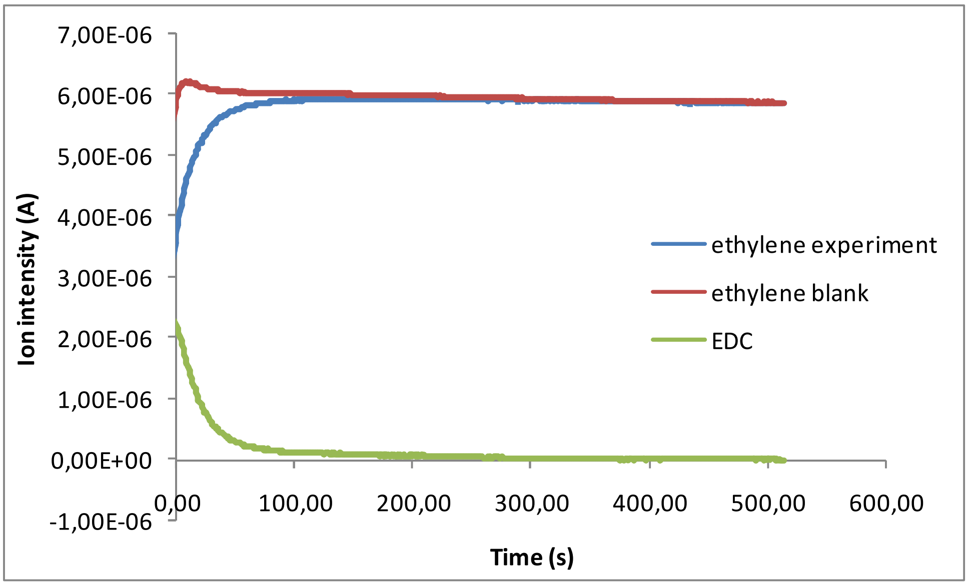

Figure C.1 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

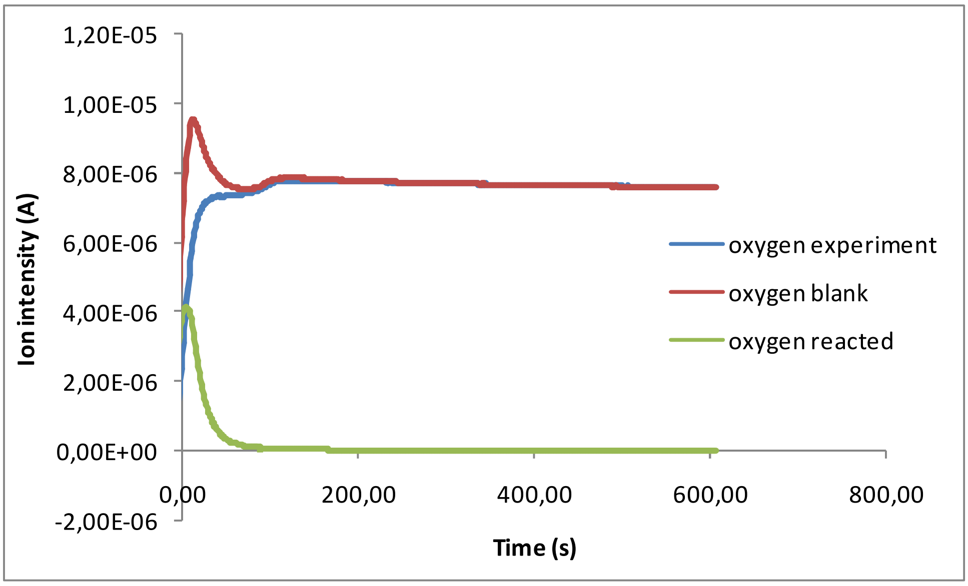

Figure C.2 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 6_2 data

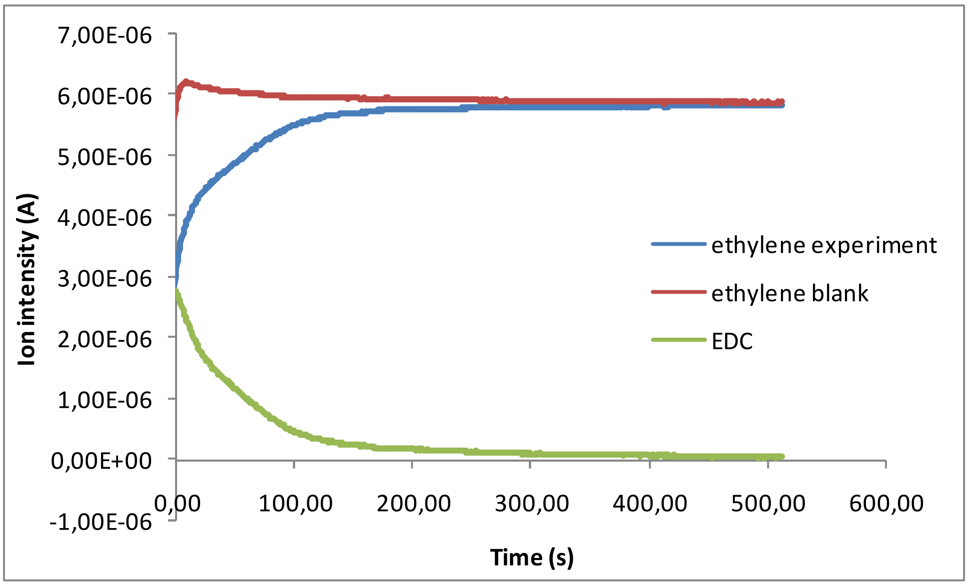

Figure C.3 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

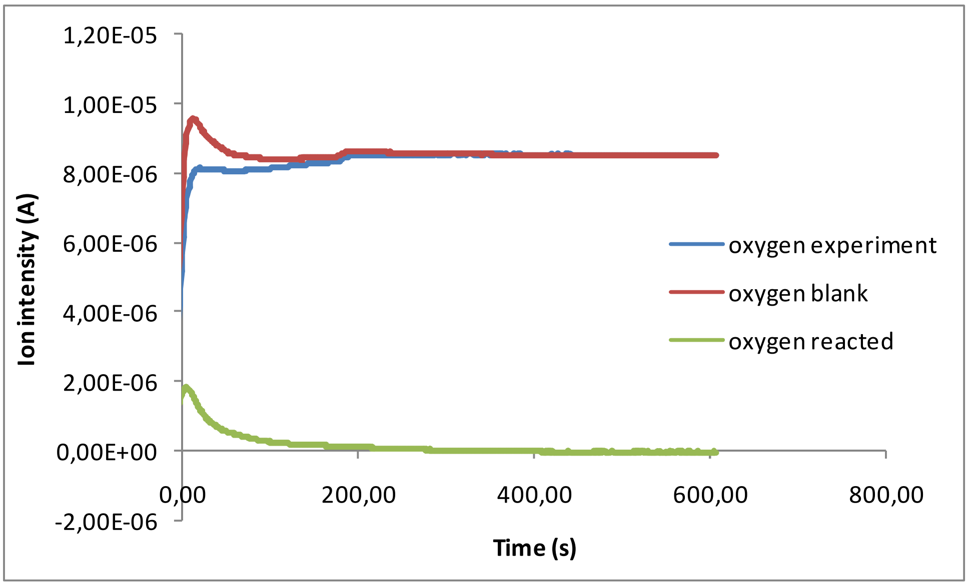

Figure C.4 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 6_3 data

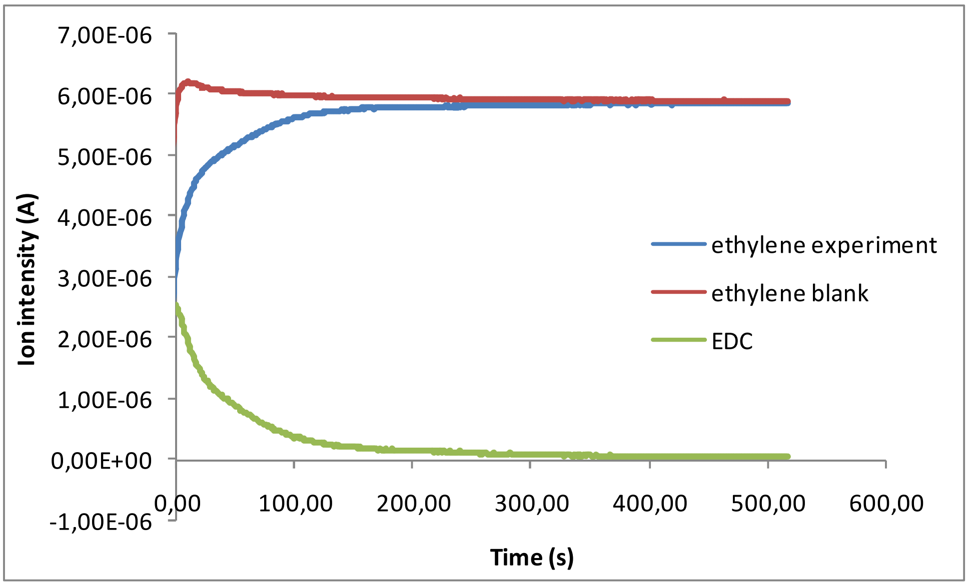

Figure C.5 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

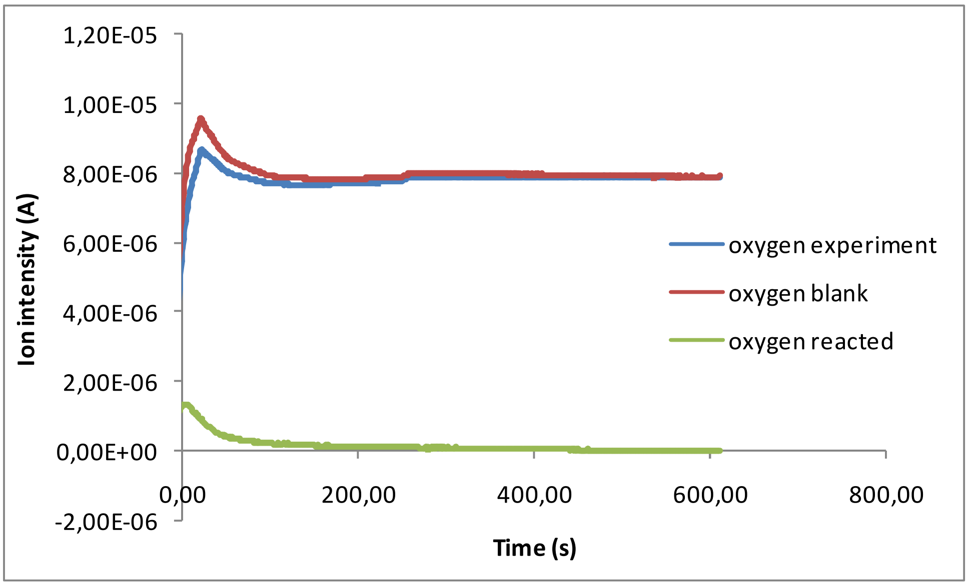

Figure C.6 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 6_4 data

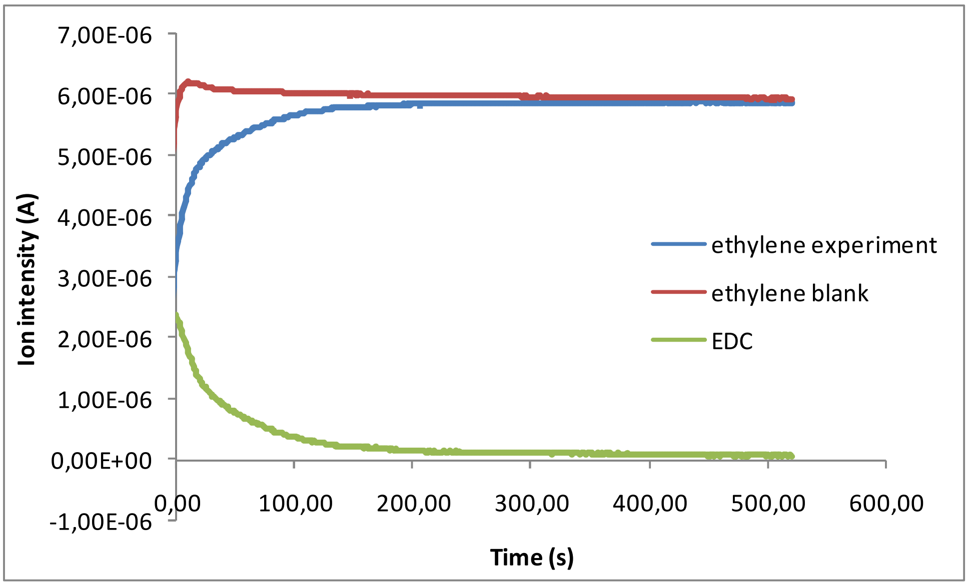

Figure C.7 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

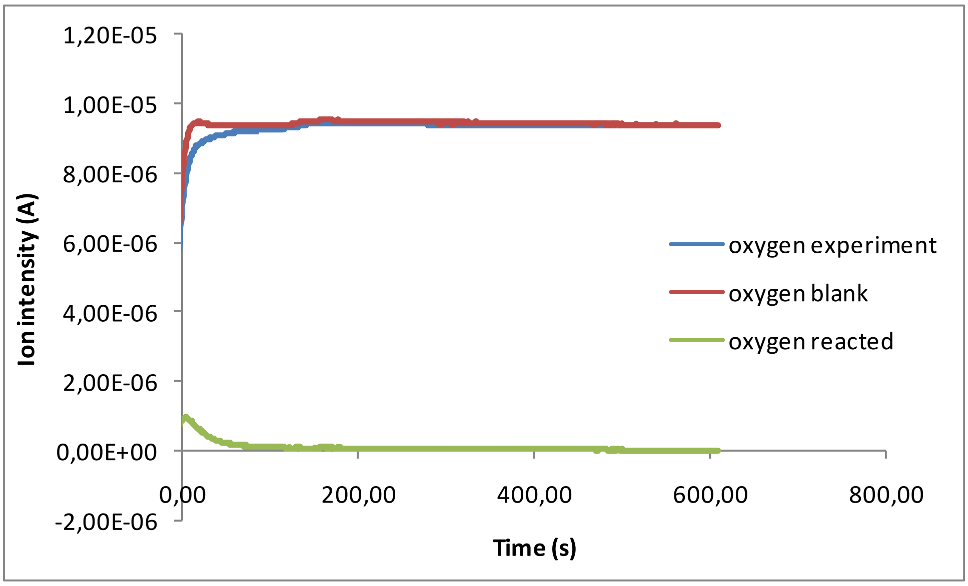

Figure C.8 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; **PO_2** = 0.177 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 6_5 data

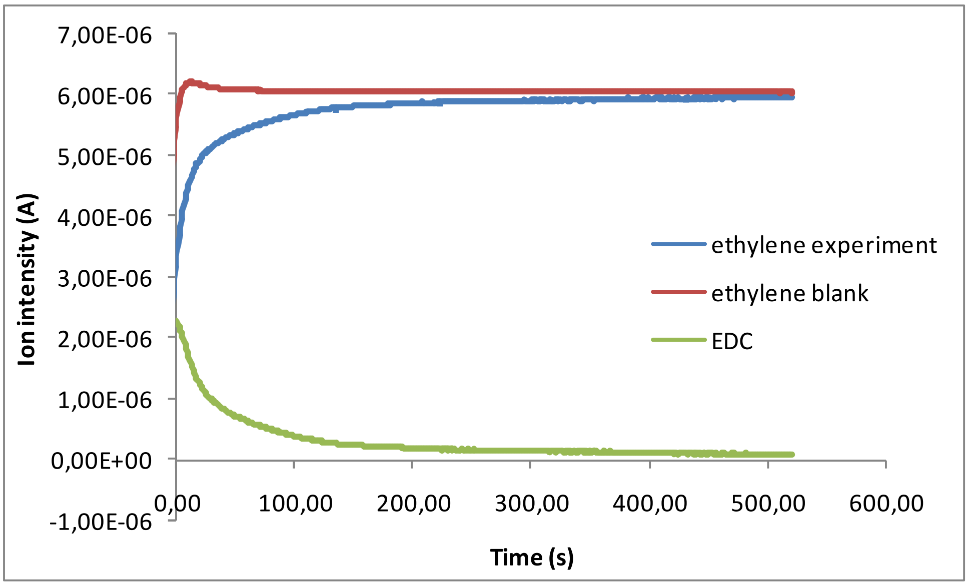

Figure C.9 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

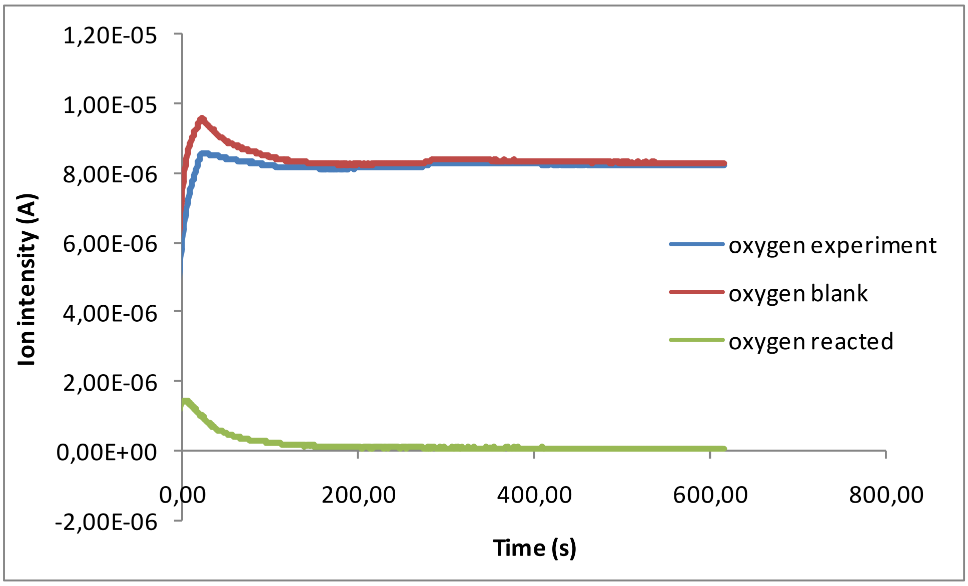

Figure C.10 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.58 ml/s; **PO_2** = 0.147 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 6_6 data

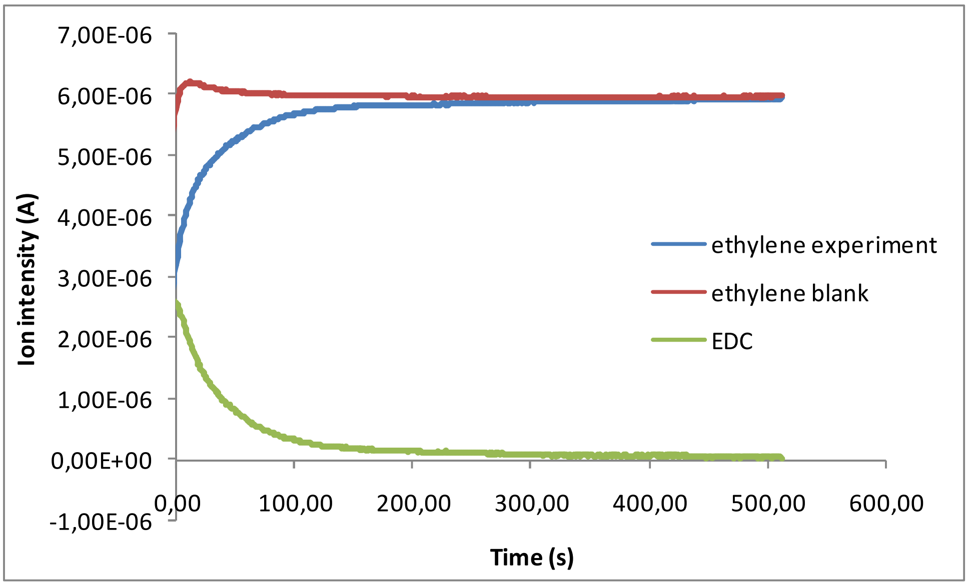

Figure C.11 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

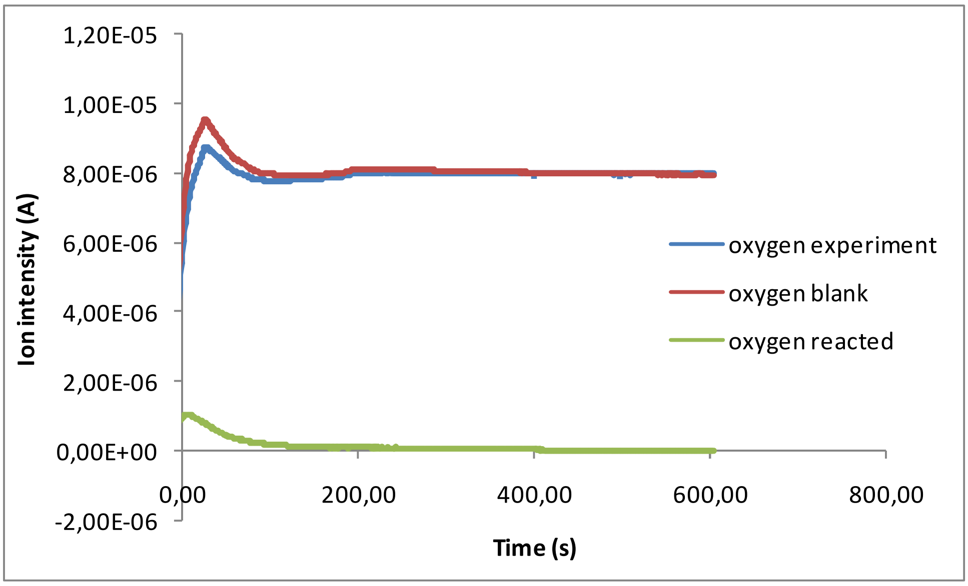

Figure C.12 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.565 g_{cat}.

Experiment 9_1 data

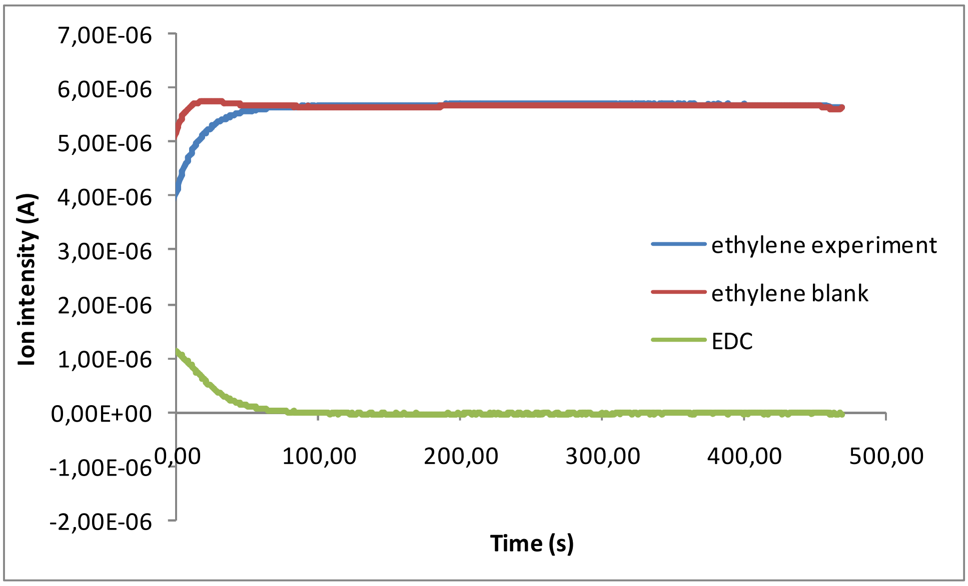

Figure C.13 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

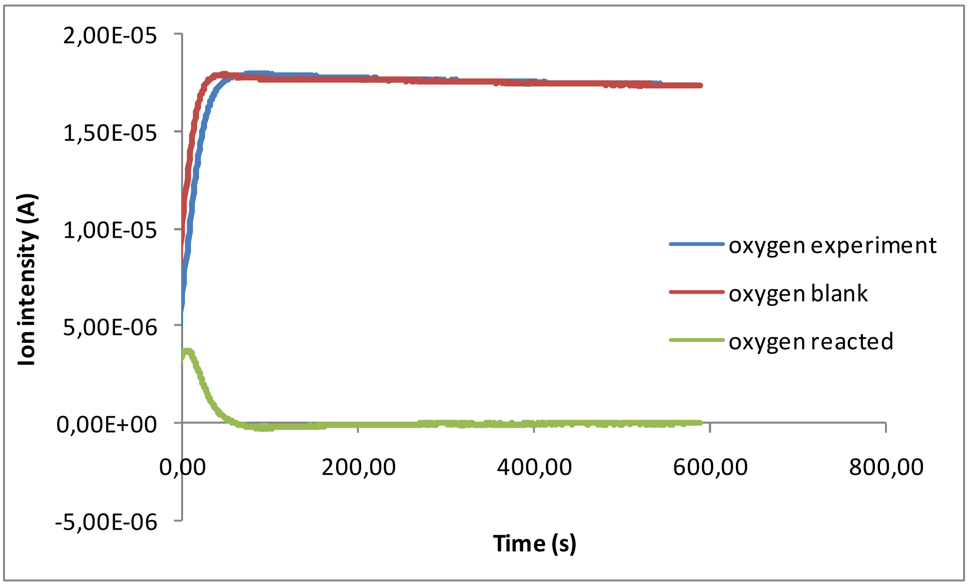

Figure C.14 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.74 ml/s; **PO_2** = 0.633 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

Experiment 9_2 data

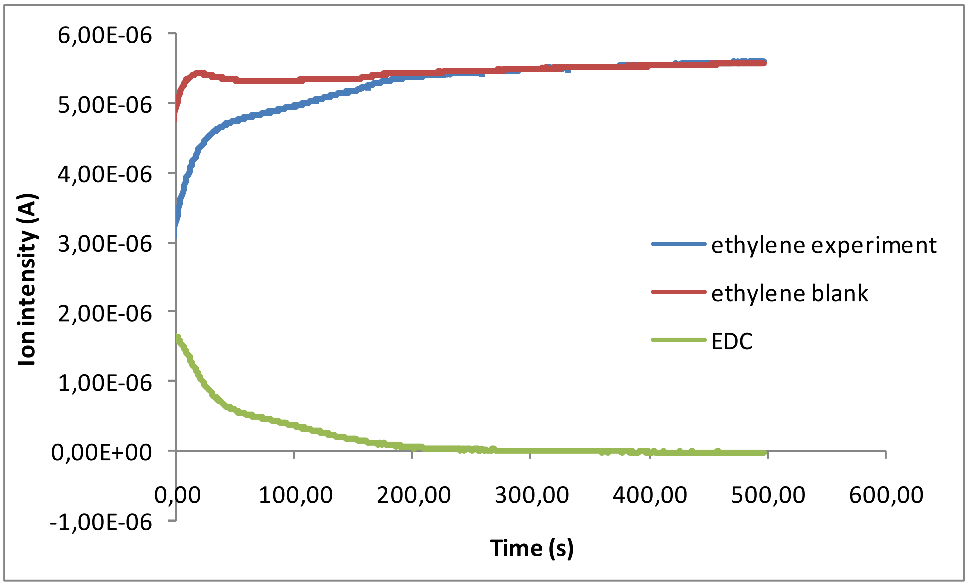

Figure C.15 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

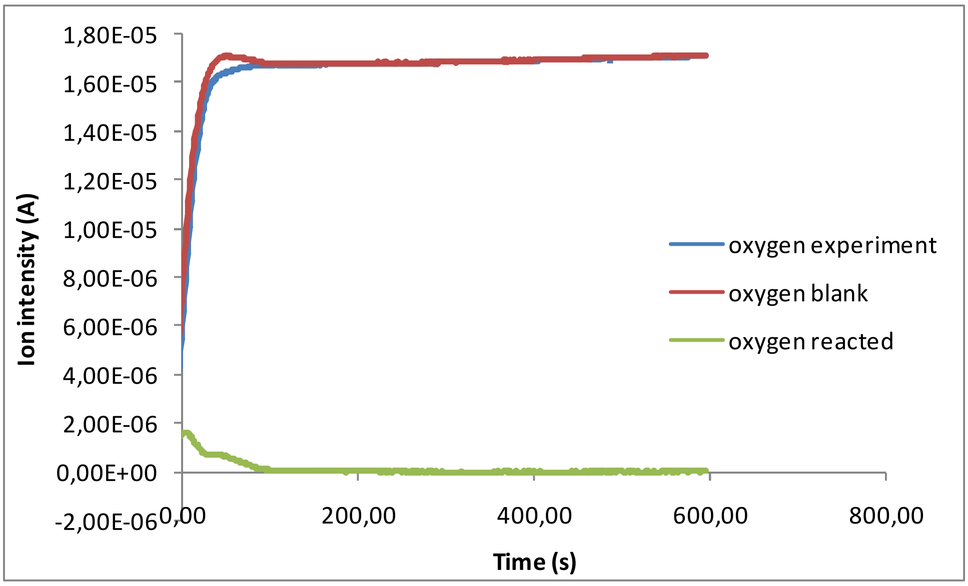

Figure C.16 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.74 ml/s; **PO_2** = 0.663 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

Experiment 9_3 data

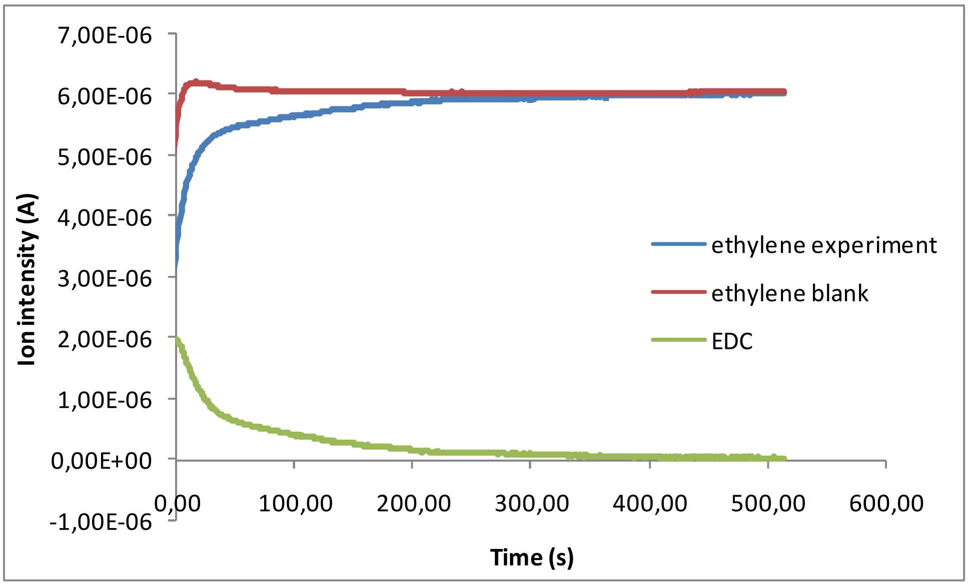

Figure C.17 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

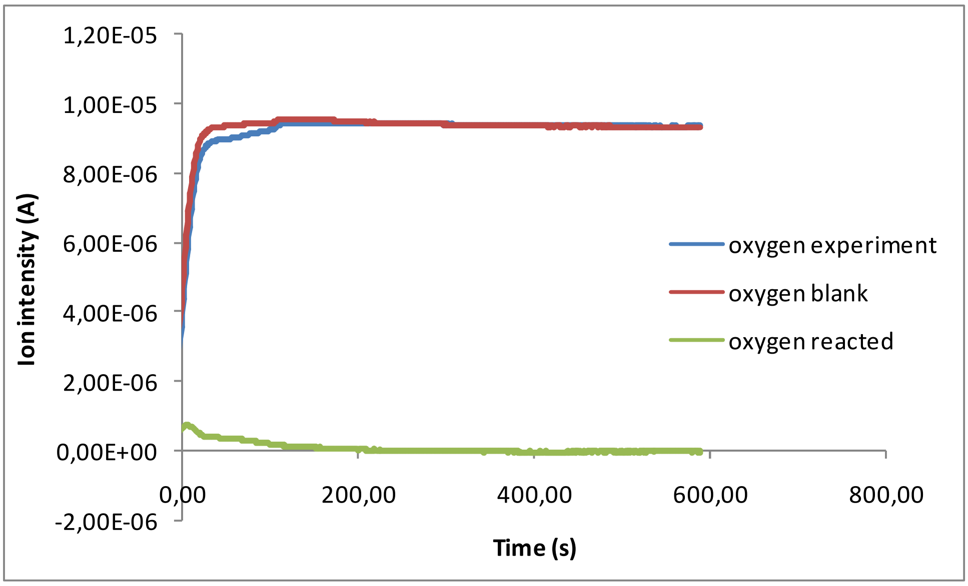

Figure C.18 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.50 ml/s; **PO_2** = 0.463 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

Experiment 9_4 data

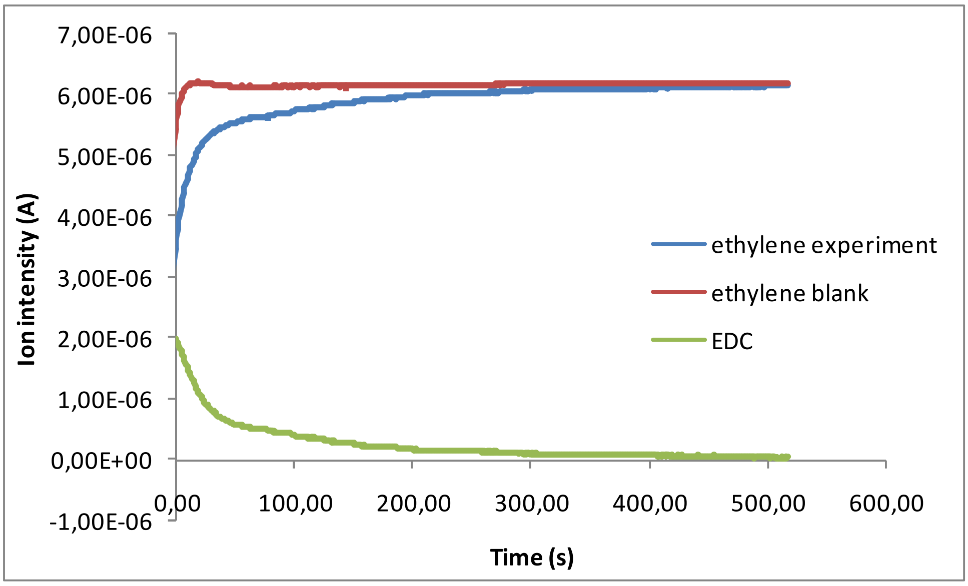

Figure C.19 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

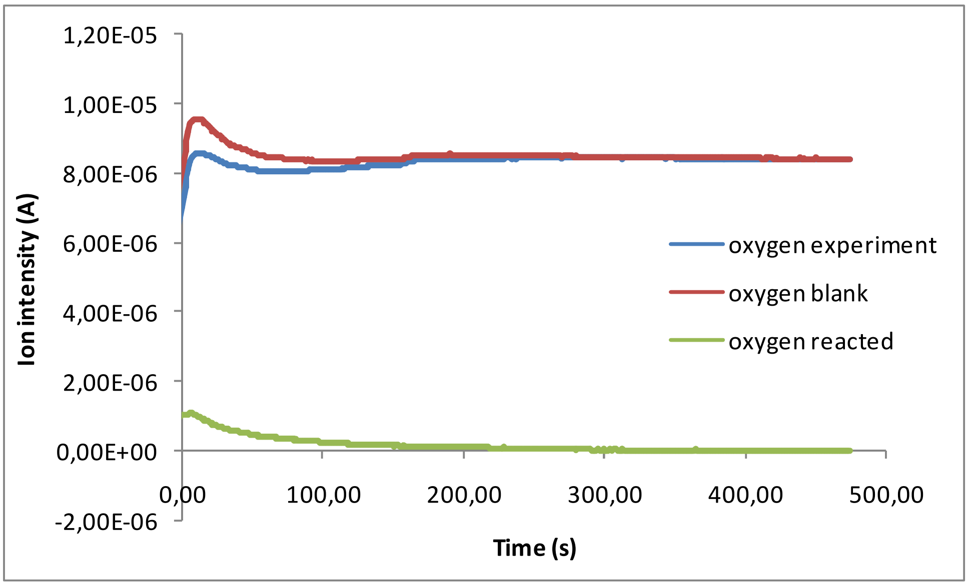

Figure C.20 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

Experiment 9_5 data

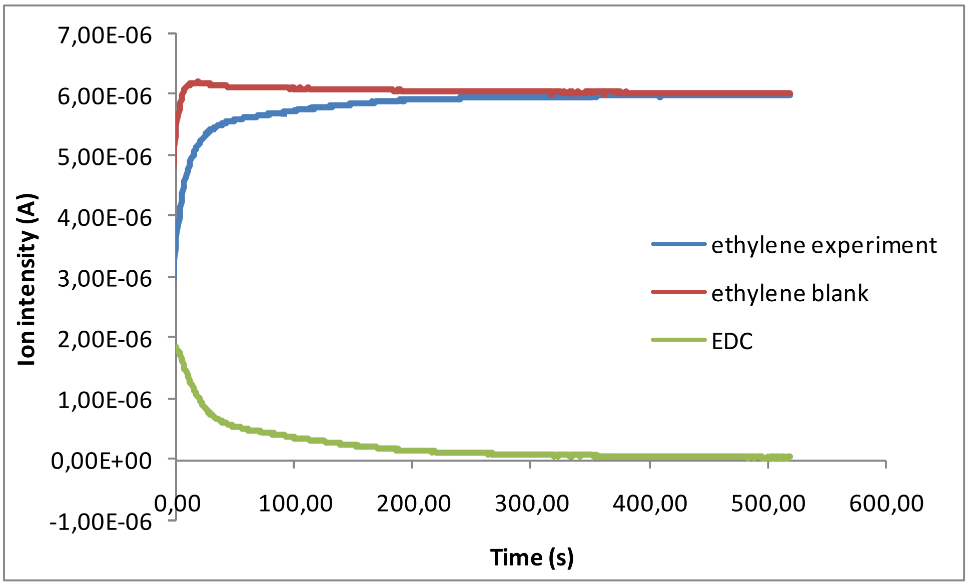

Figure C.21 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.612 ml/s; **PC_2H_4** = 0.058 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

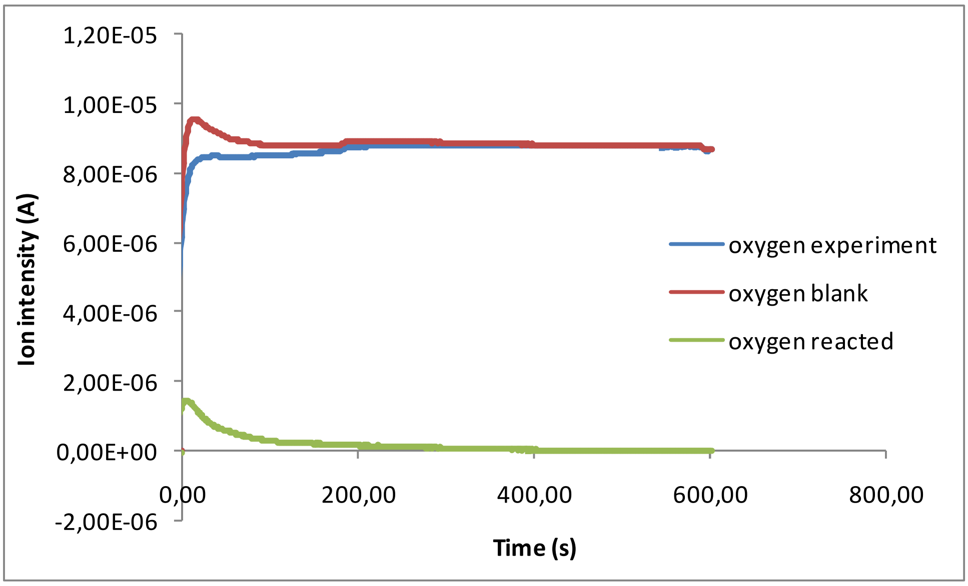

Figure C.22 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 508K; **w_{Cu}** = 5.77 g_{Cu}/g_{cat}; **m_{cat}** = 0.436 g_{cat}.

Experiment 10_1 data

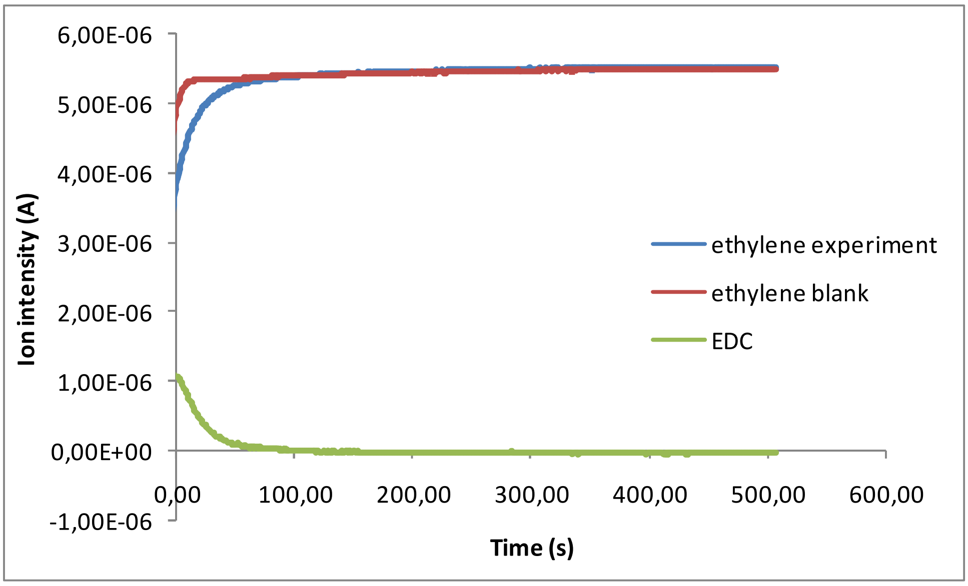

Figure C.23 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.612 ml/s; **PC_2H_4** = 0.058 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

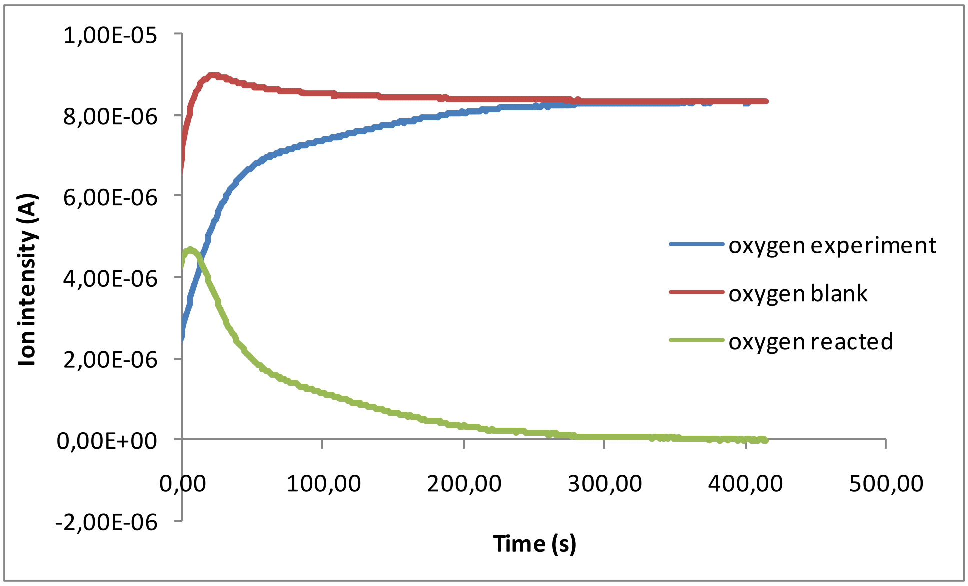

Figure C.24 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.233 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

Experiment 10_2 data

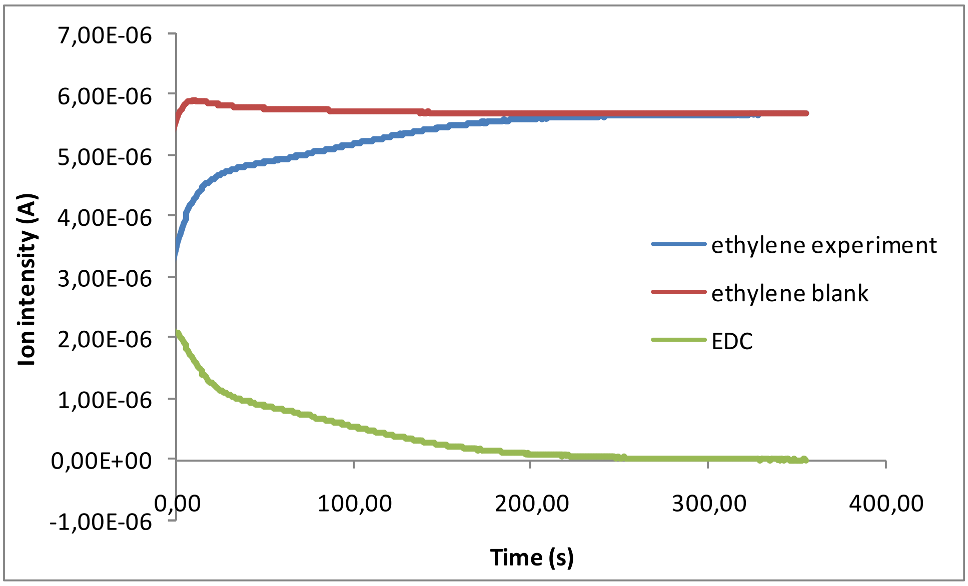

Figure C.25 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.612 ml/s; $\mathbf{PC_2H_4}$ = 0.058 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.732 g_{cat}.

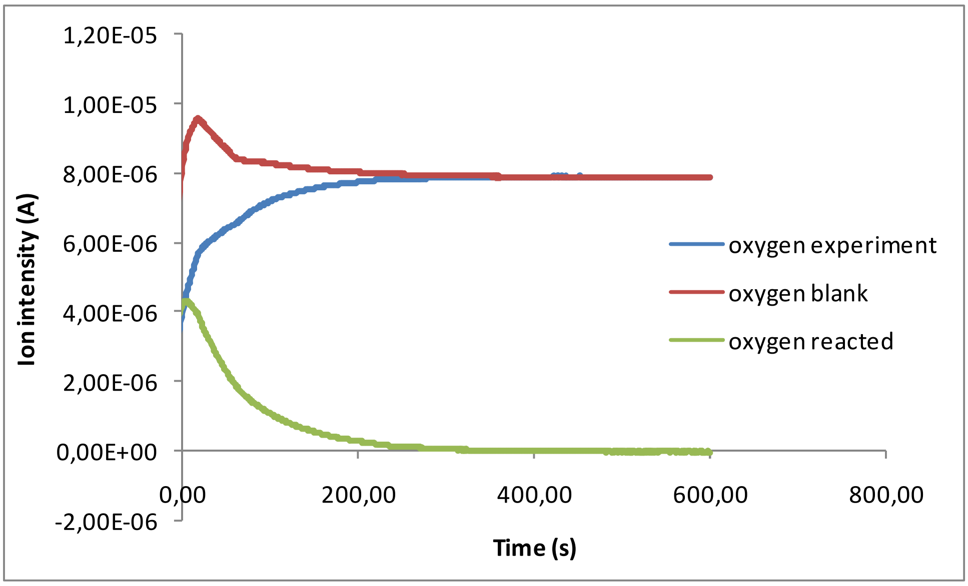

Figure C.26 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; $\mathbf{PO_2}$ = 0.223 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.732 g_{cat}.

Experiment 10_3 data

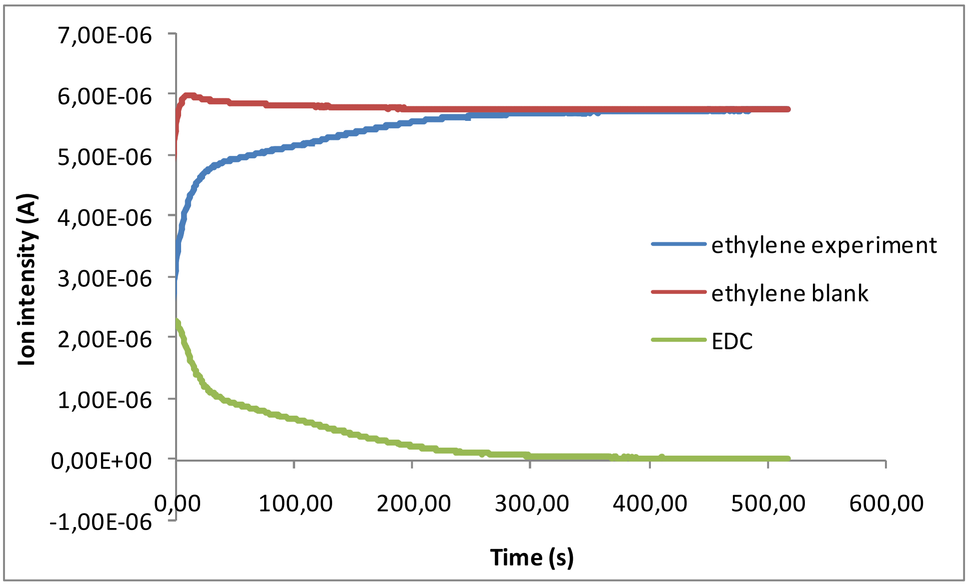

Figure C.27 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; $\mathbf{PC_2H_4}$ = 0.065 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.732 g_{cat}.

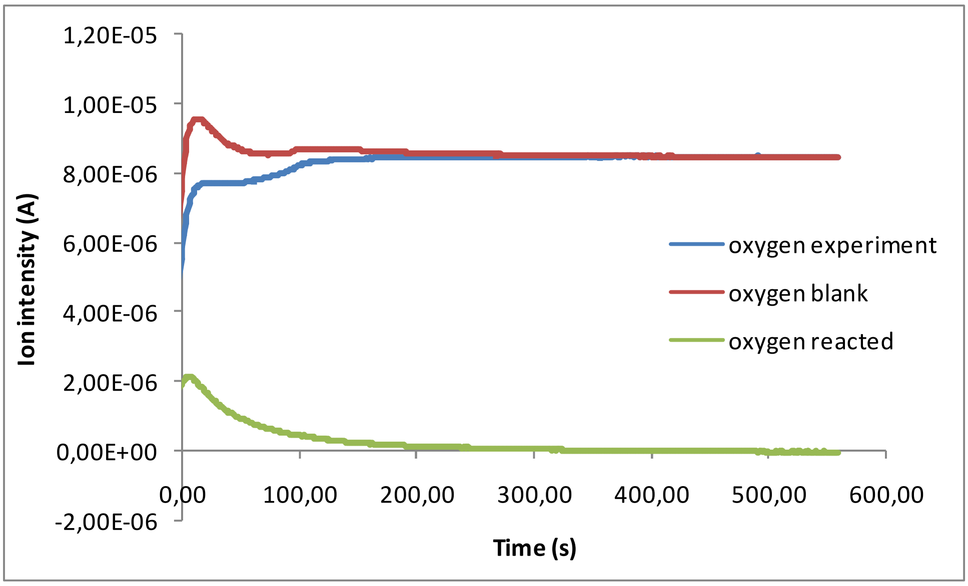

Figure C.28 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; $\mathbf{PO_2}$ = 0.301 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.732 g_{cat}.

Experiment 10_4 data

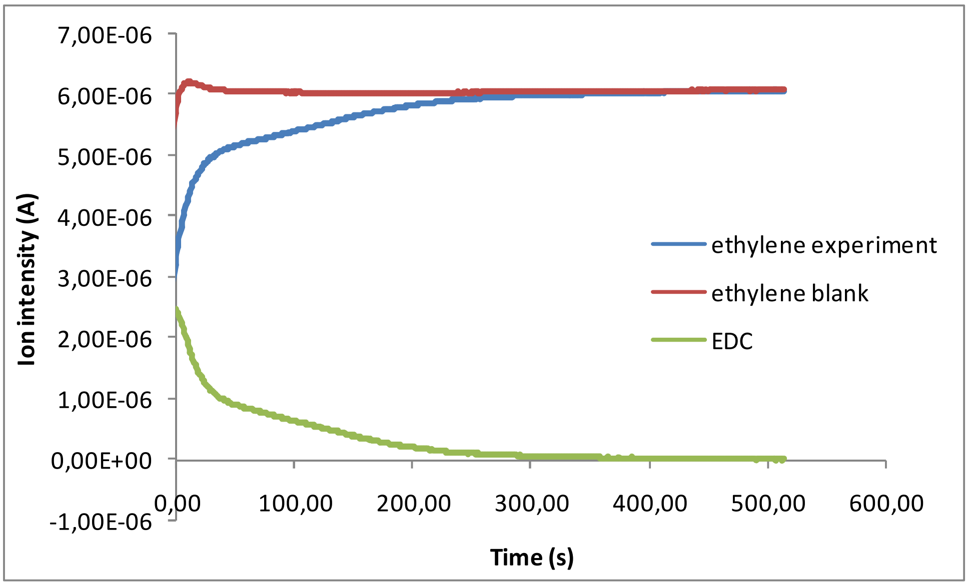

Figure C.29 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

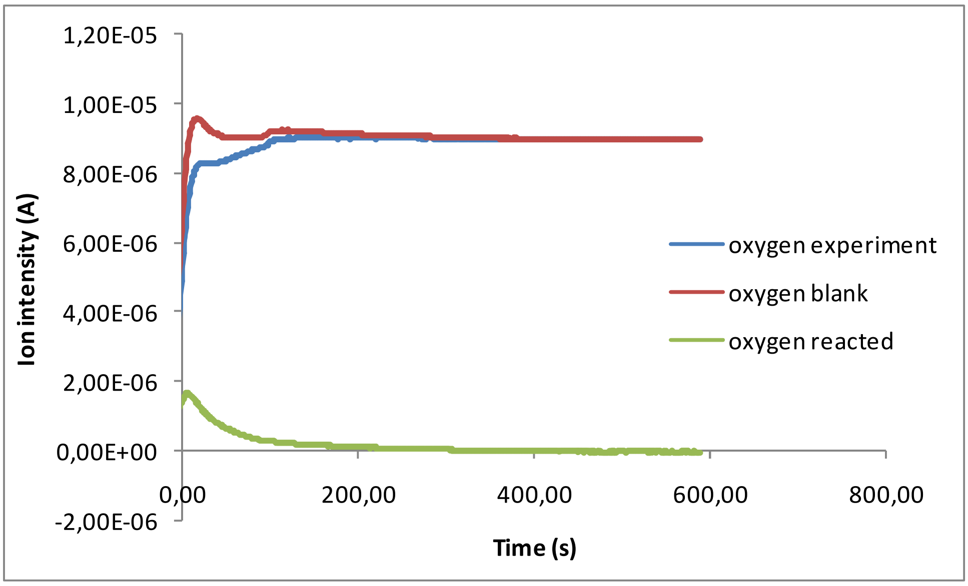

Figure C.30 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.5 ml/s; **PO_2** = 0.463 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

Experiment 10_5 data

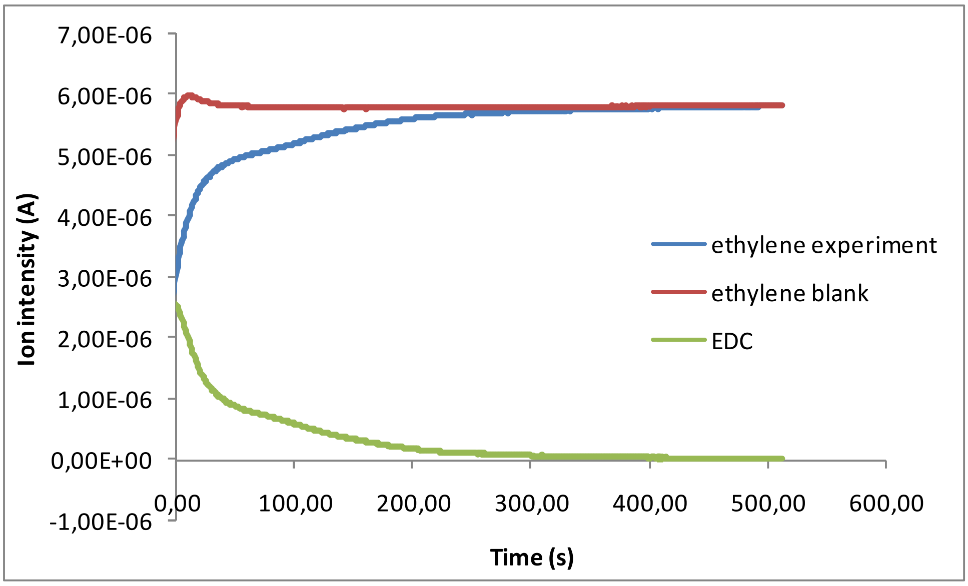

Figure C.31 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

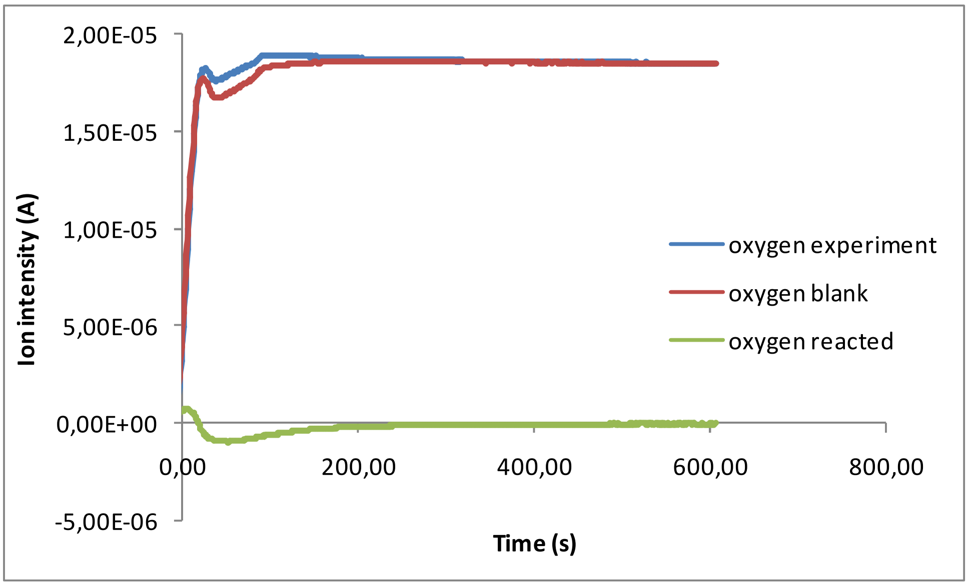

Figure C.32 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.74 ml/s; **PO_2** = 0.633 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.732 g_{cat}.

Experiment 11_2 data

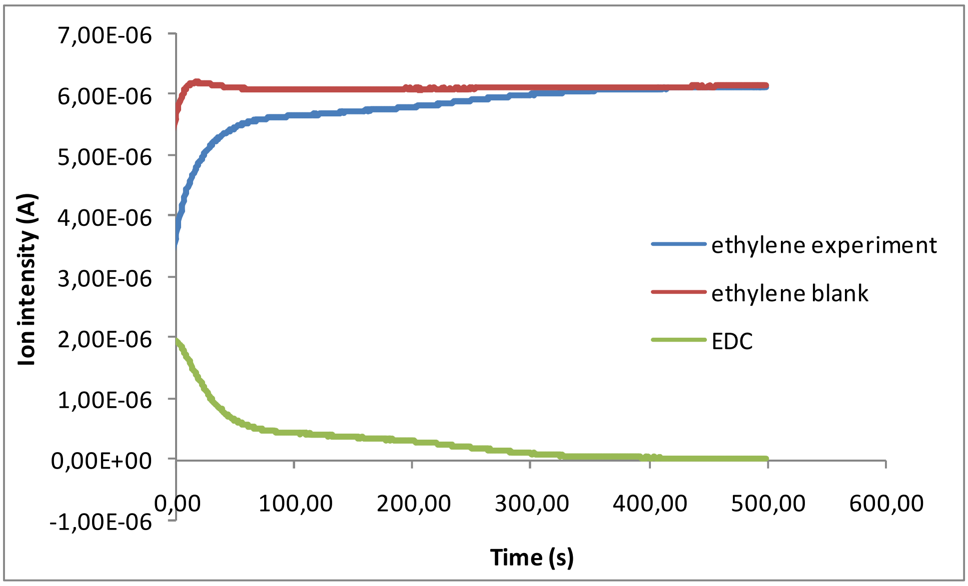

Figure C.33 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

Experiment 11_3 data

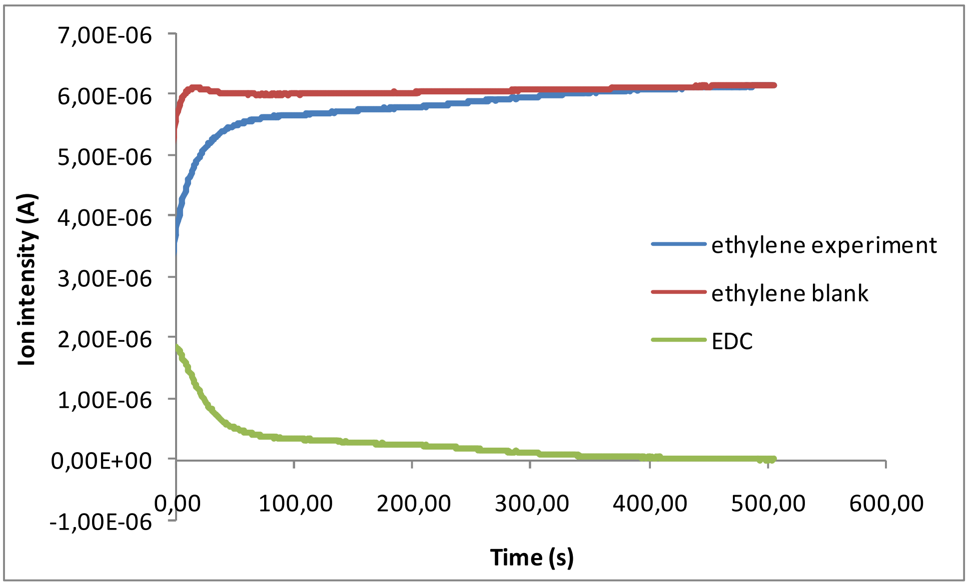

Figure C.34 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

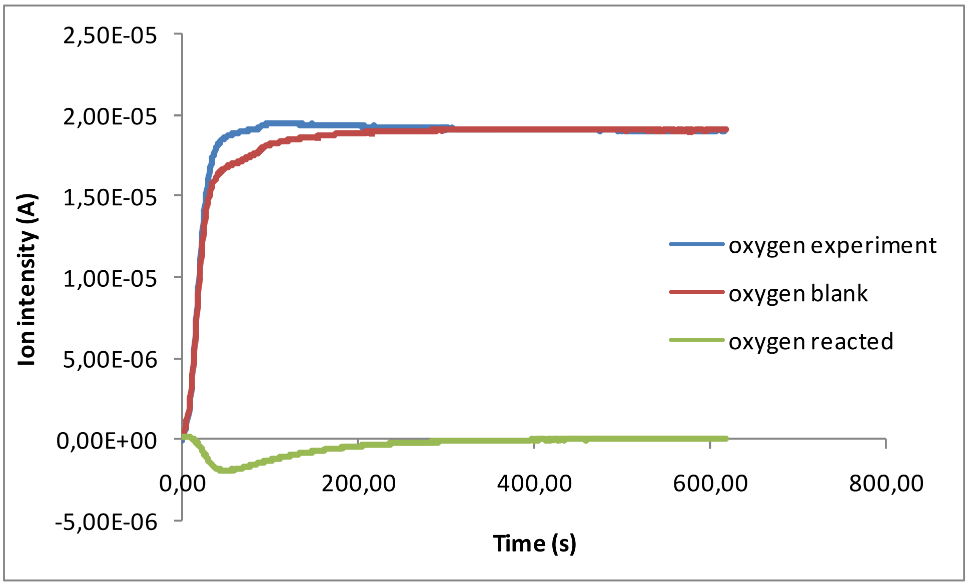

Figure C.35 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.74 ml/s; **PO_2** = 0.663 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

Experiment 11_4 data

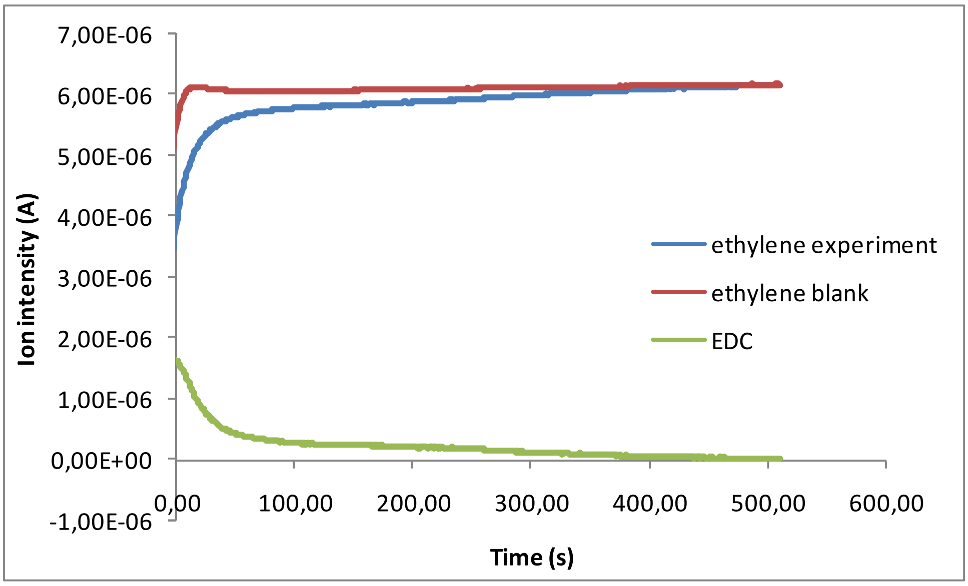

Figure C.36 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

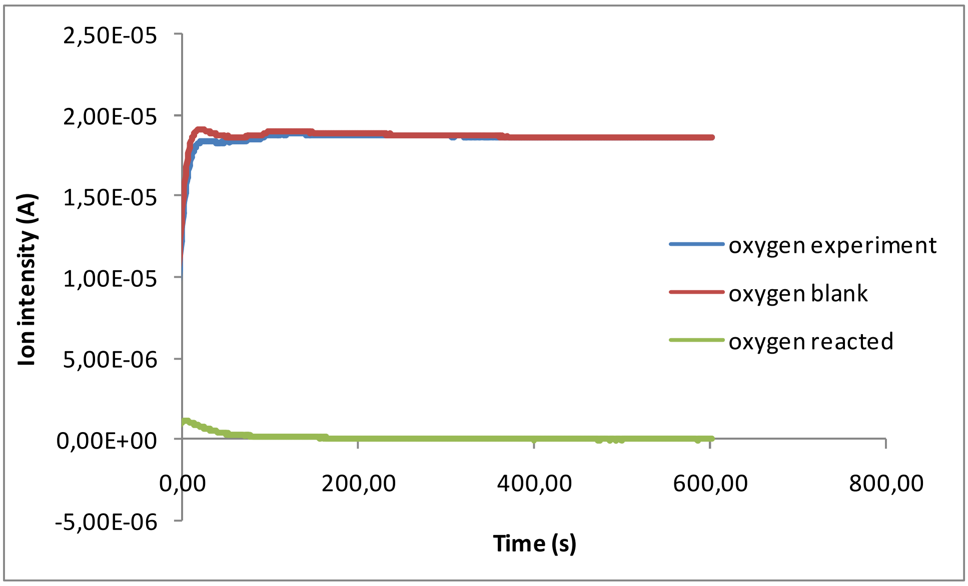

Figure C.37 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.01 ml/s; **PO_2** = 0.463 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

Experiment 11_5 data

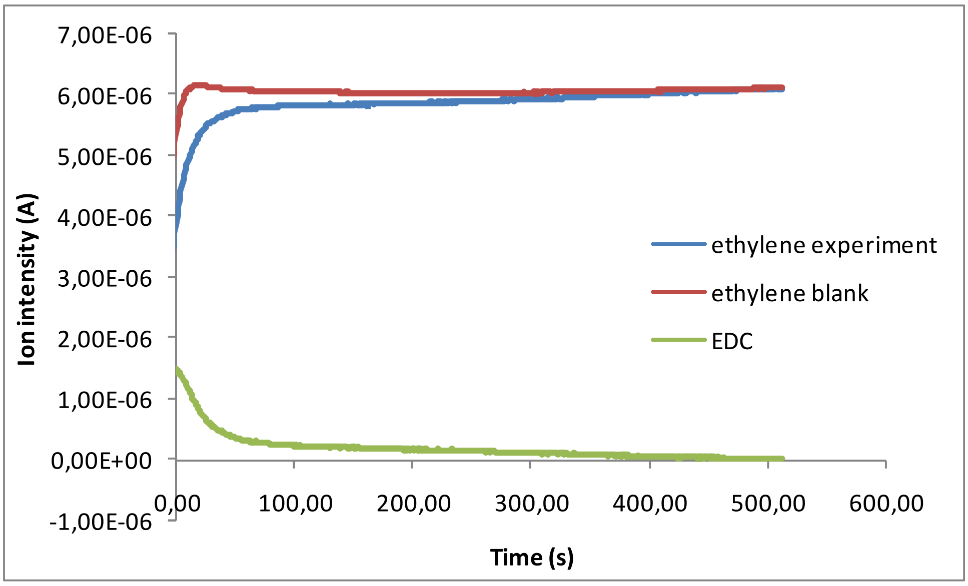

Figure C.38 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

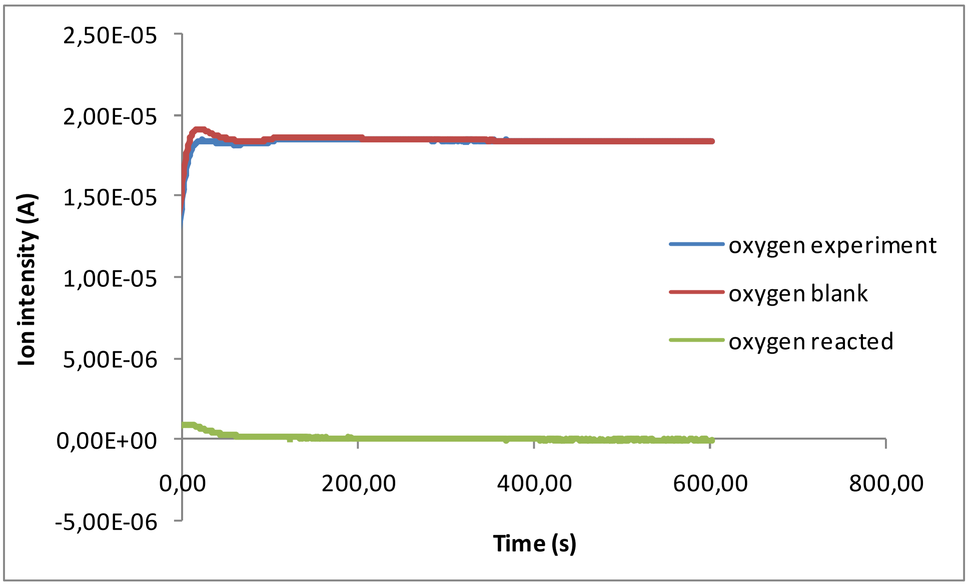

Figure C.39 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.28 ml/s; **PO_2** = 0.365 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.498 g_{cat}.

Experiment 12_2 data

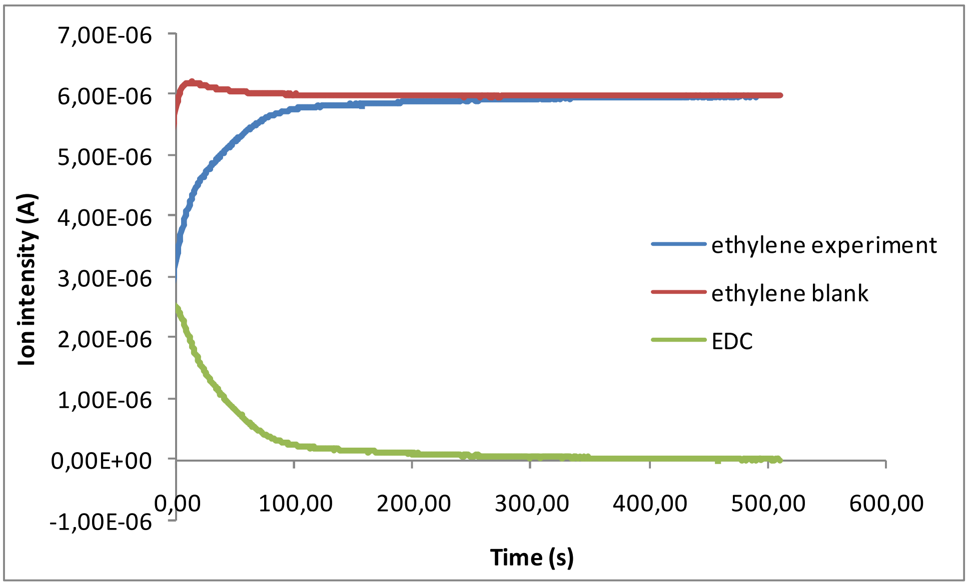

Figure C.40 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; $\mathbf{PC_2H_4}$ = 0.073 atm; **T** = 523K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.490 g_{cat}.

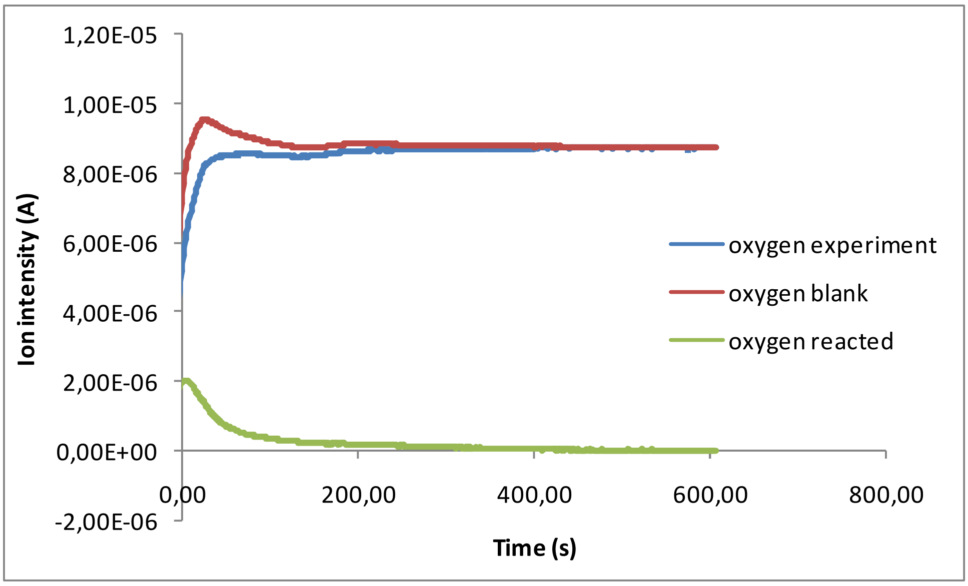

Figure C.41 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; $\mathbf{PO_2}$ = 0.177 atm; **T** = 523K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.490 g_{cat}.

Experiment 12_3 data

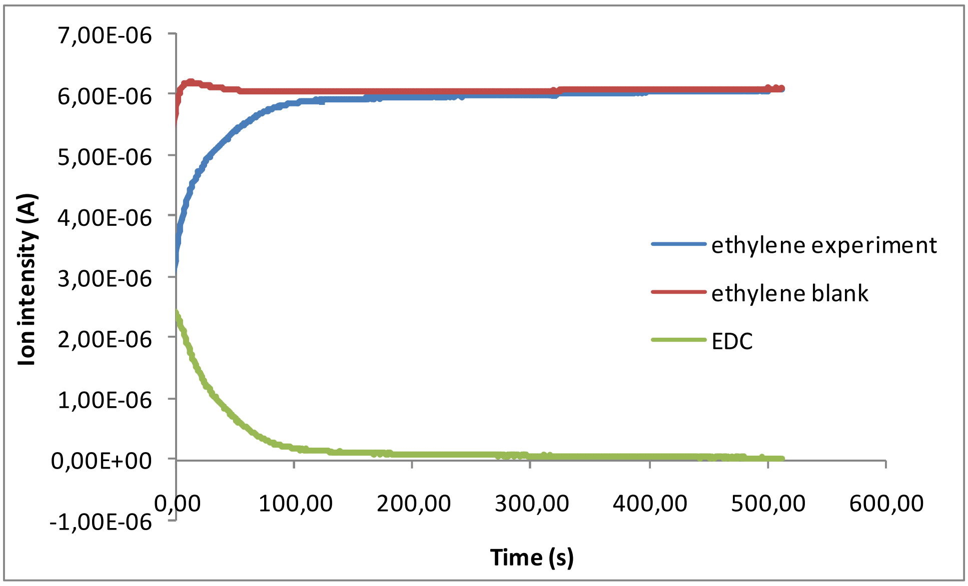

Figure C.42 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

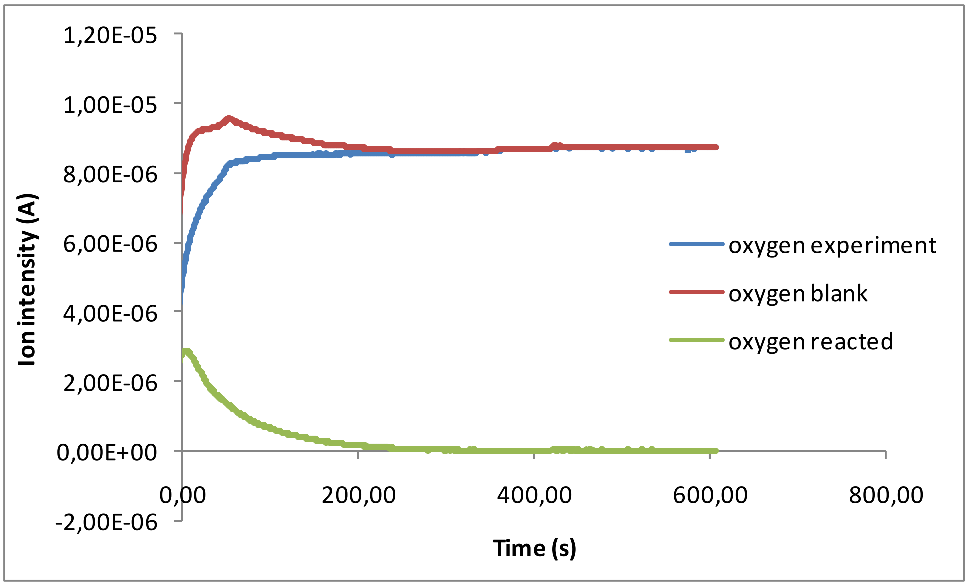

Figure C.43 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; **PO_2** = 0.177 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 12_4 data

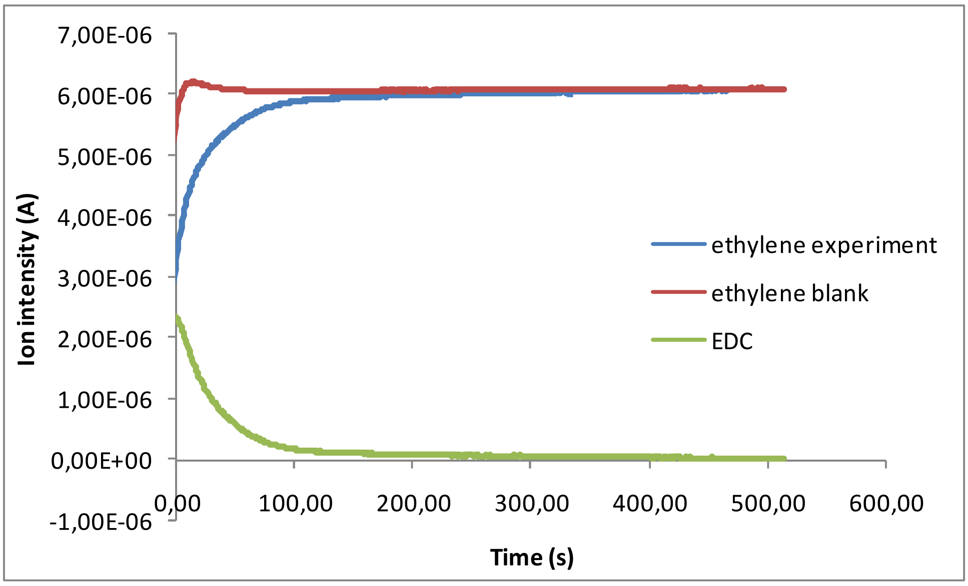

Figure C.44 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

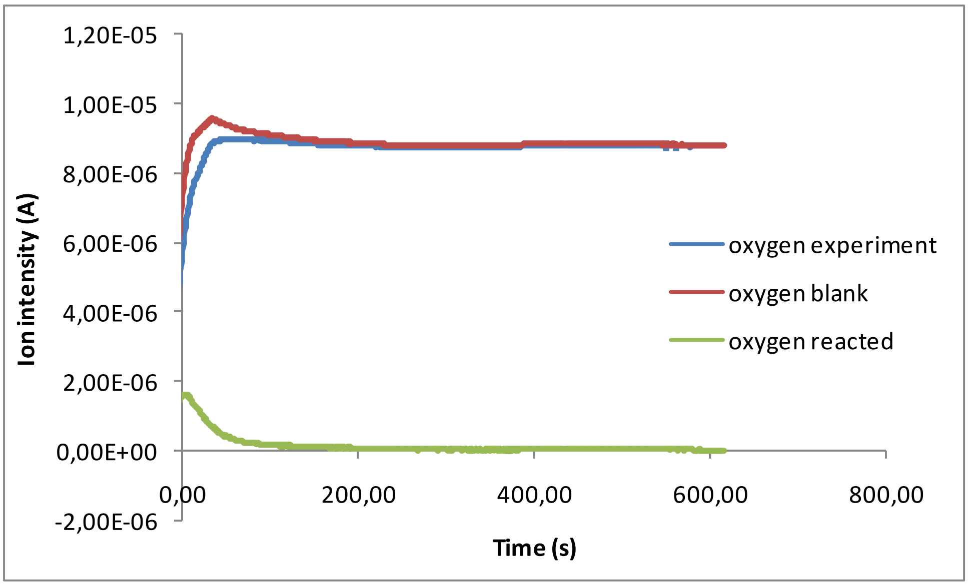

Figure C.45 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; **PO_2** = 0.177 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 12_5 data

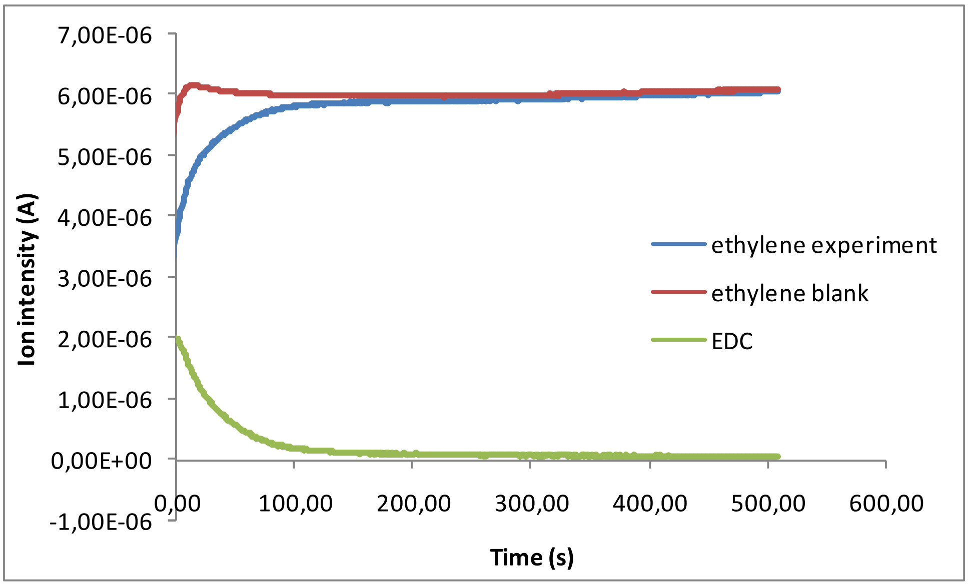

Figure C.46 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

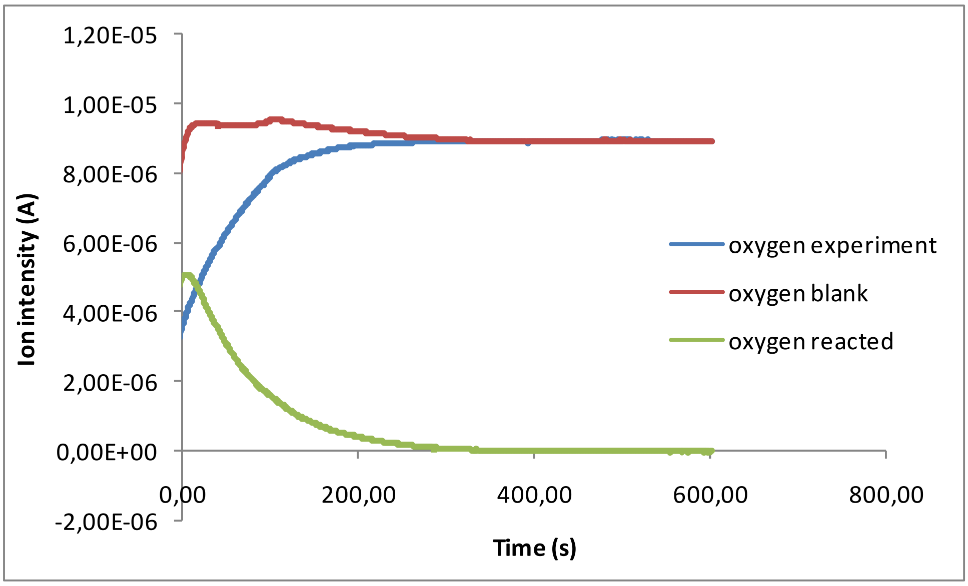

Figure C.47 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.58 ml/s; **PO_2** = 0.147 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 12_6 data

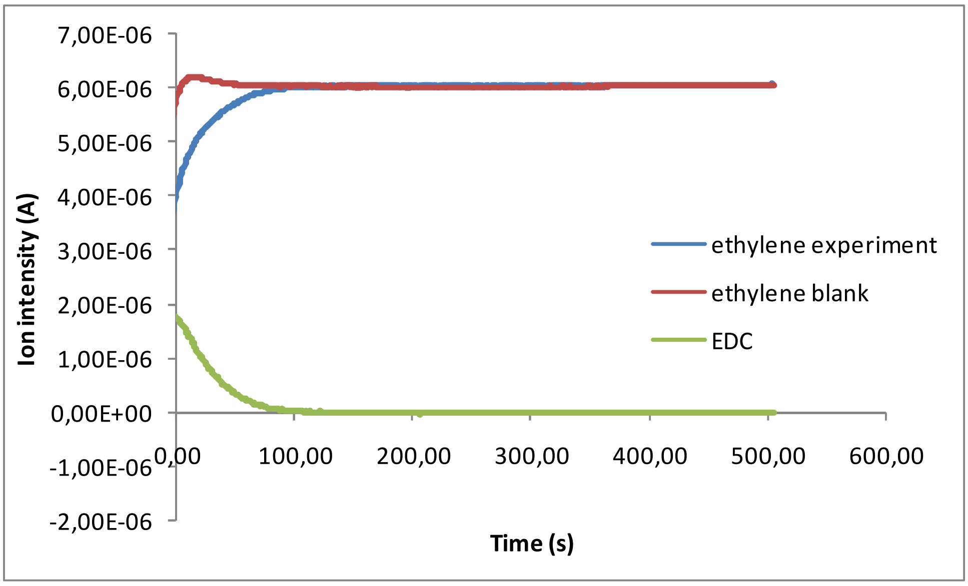

Figure C.48 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

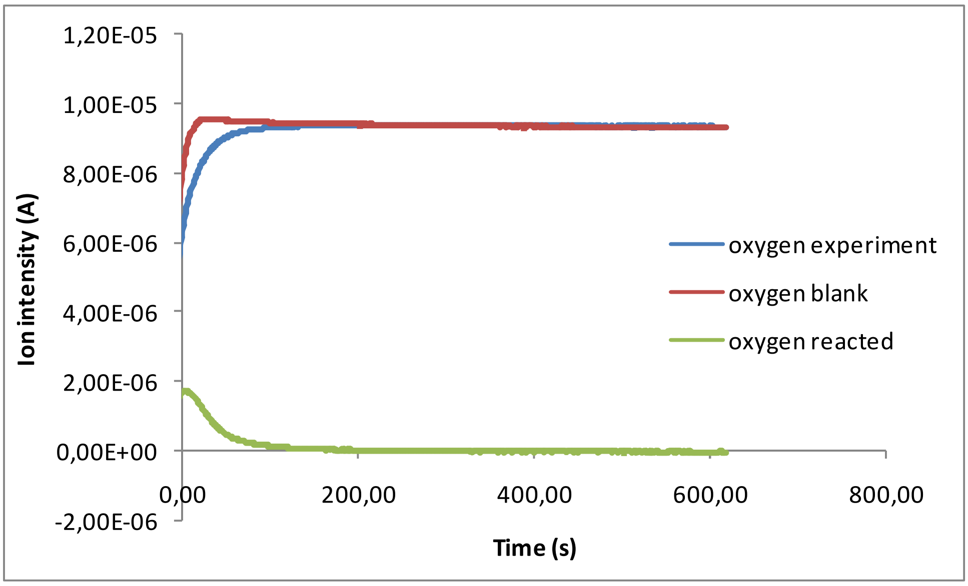

Figure C.49 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.58 ml/s; **PO_2** = 0.147 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 12_7 data

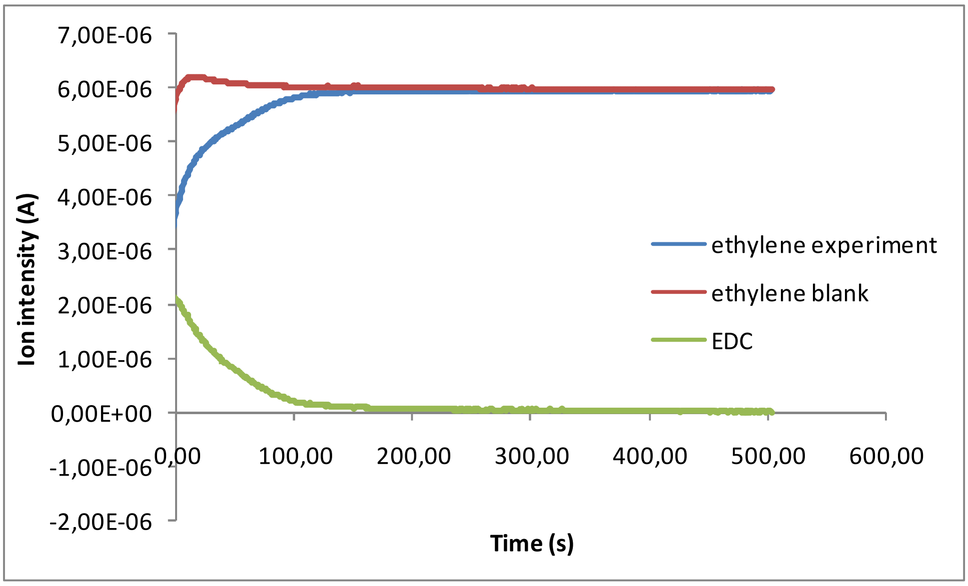

Figure C.50 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

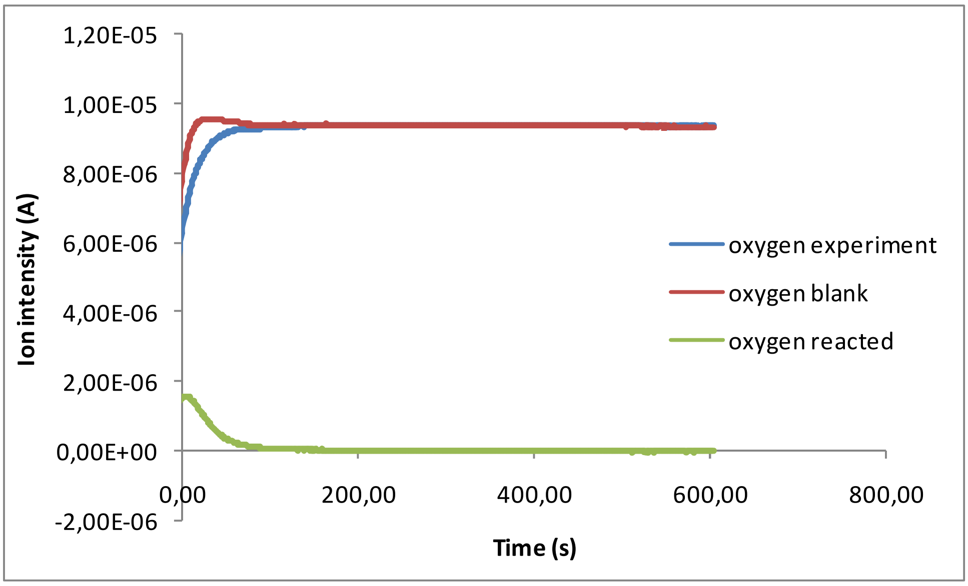

Figure C.51 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.58 ml/s; **PO_2** = 0.147 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 12_8 data

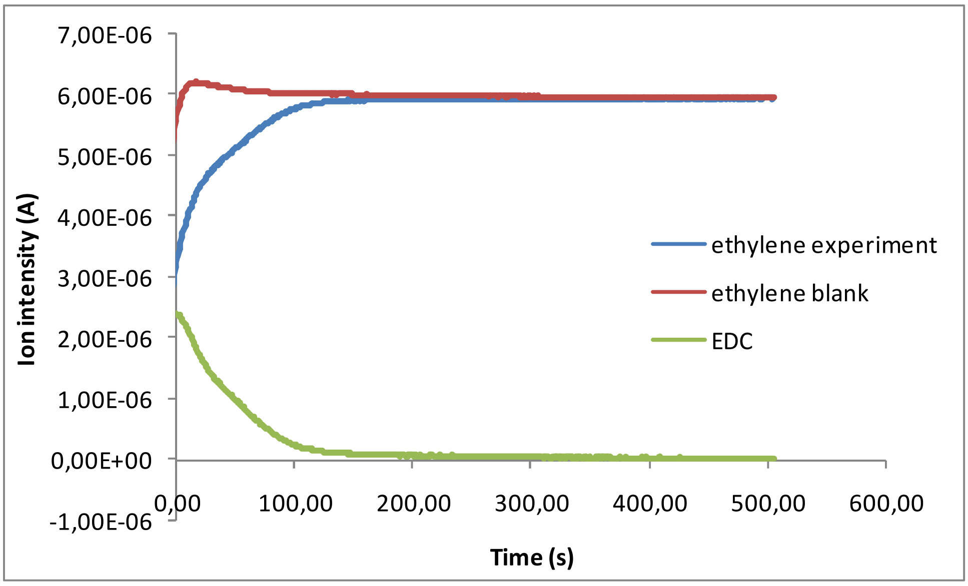

Figure C.52 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 523K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.490 g_{cat}.

Experiment 13_1 data

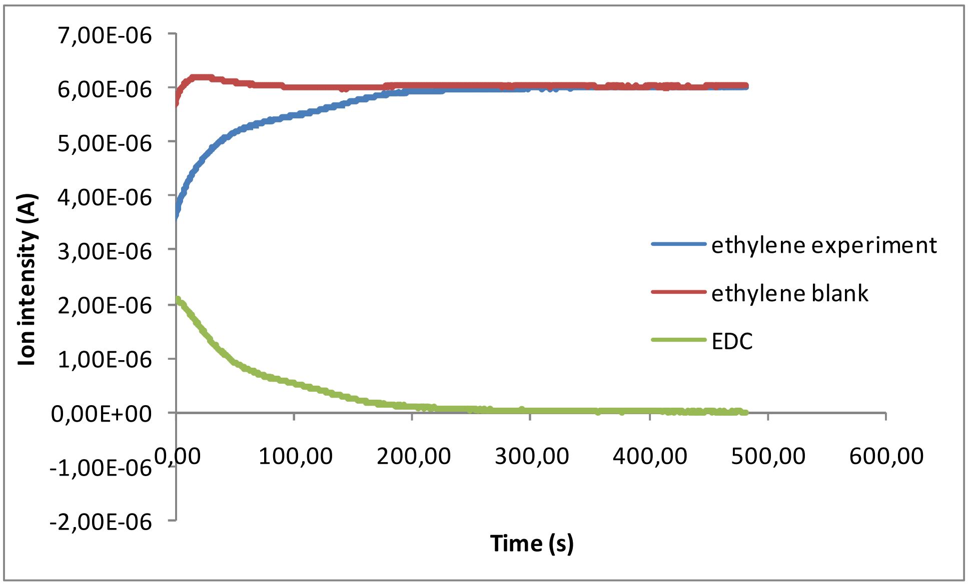

Figure C.53 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC₂H₄** = 0.1 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.556 g_{cat}.

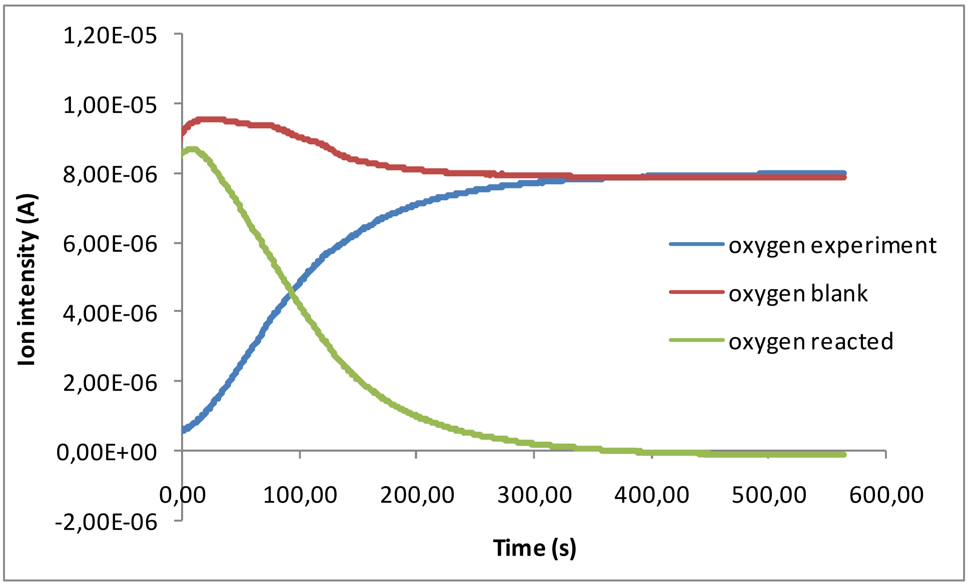

Figure C.54 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; $\mathbf{PO_2}$ = 0.223 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.556 g_{cat}.

Experiment 13_2 data

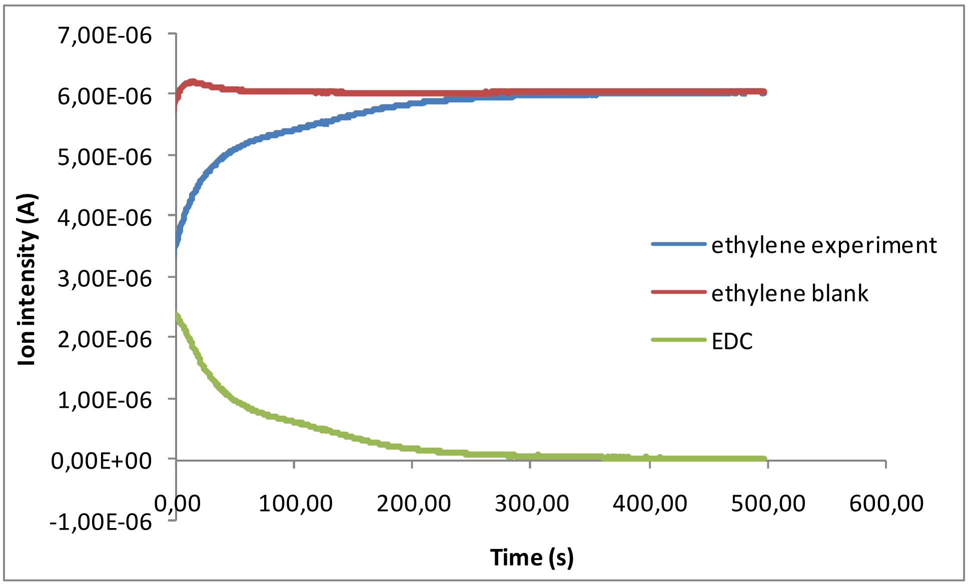

Figure C.55 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

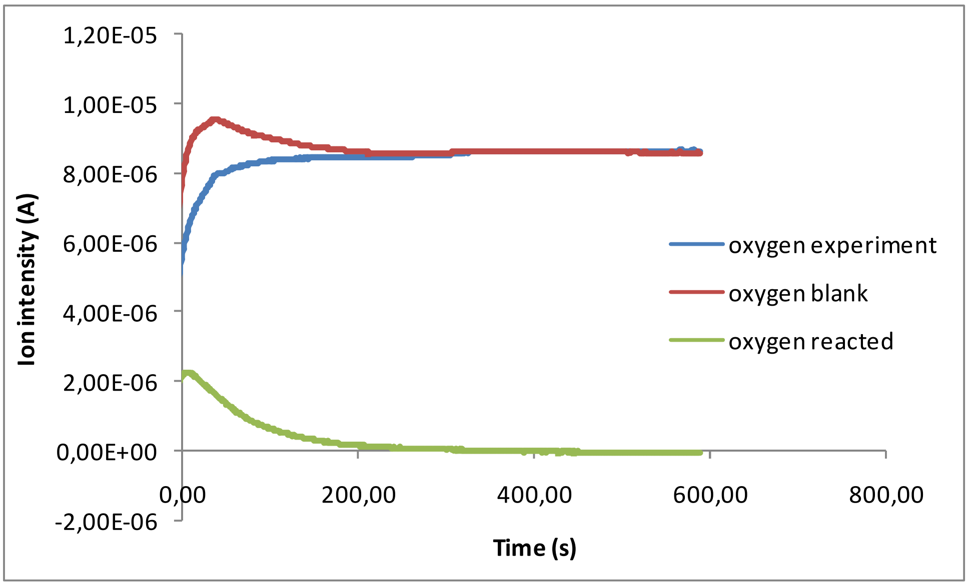

Figure C.56 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

Experiment 13_3 data

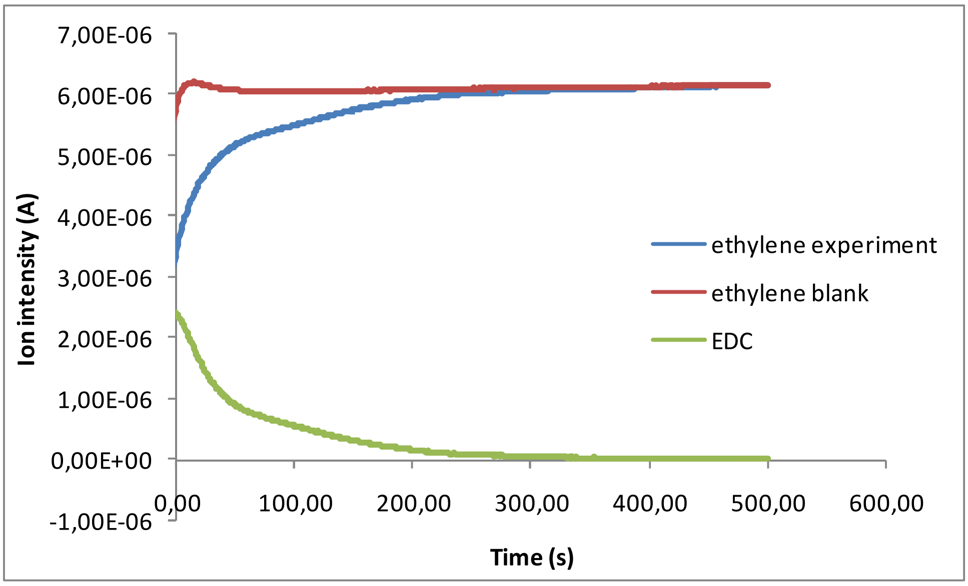

Figure C.57 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

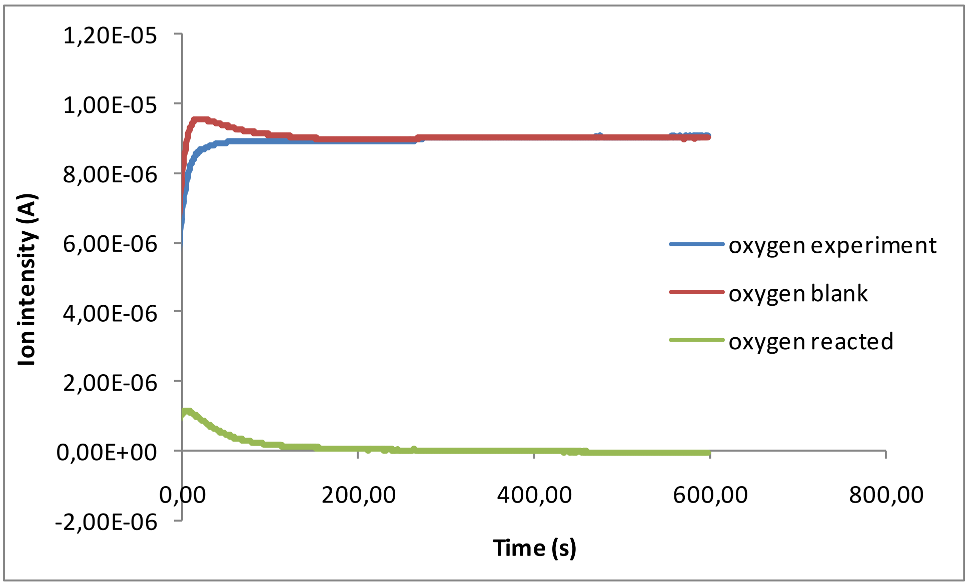

Figure C.58 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

Experiment 13_4 data

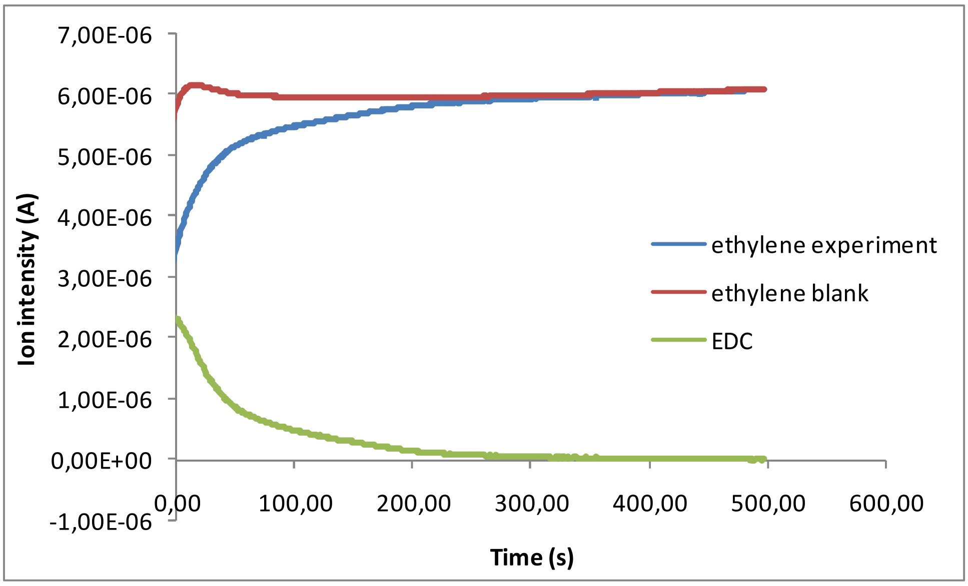

Figure C.59 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

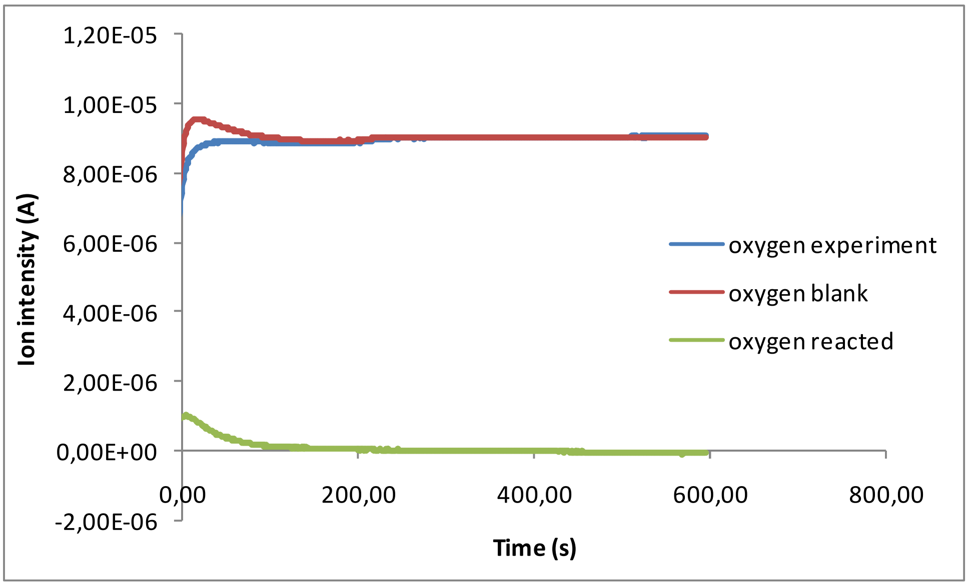

Figure C.60 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

Experiment 13_5 data

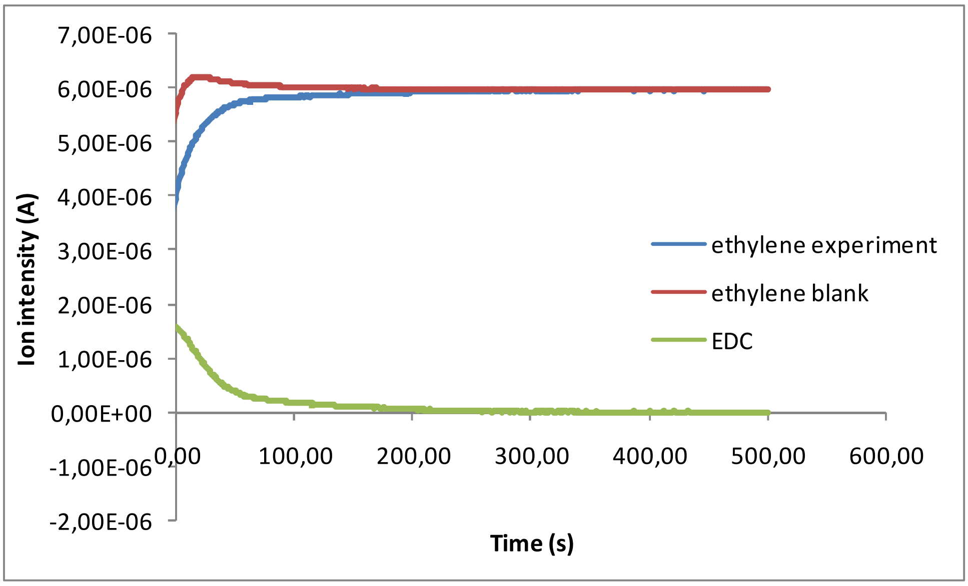

Figure C.61 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC$_2$H$_4$** = 0.1 atm; **T** = 493K; **w$_{Cu}$** = 6.11 g$_{Cu}$/g$_{cat}$; **m$_{cat}$** = 0.556 g$_{cat}$.

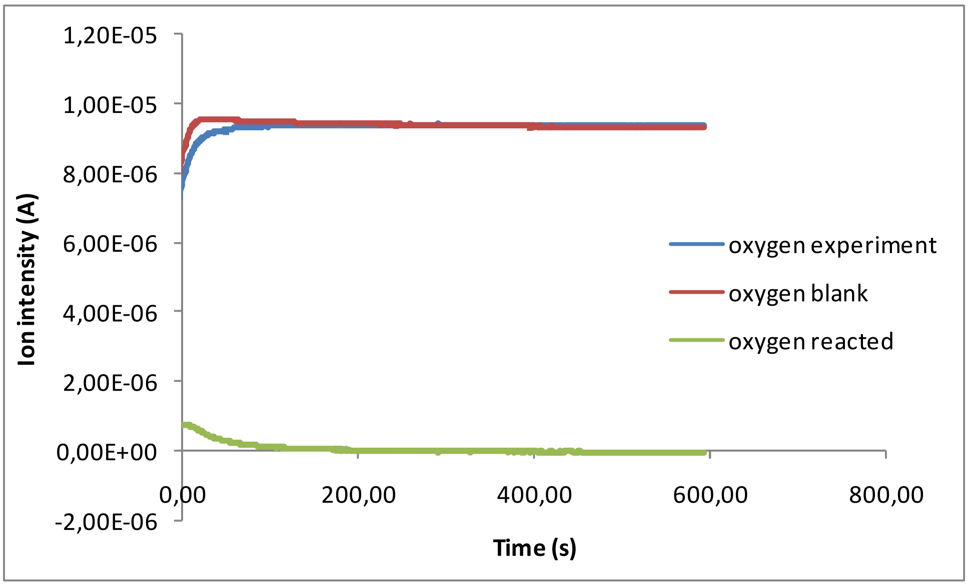

Figure C.62 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO$_2$** = 0.223 atm; **T** = 493K; **w$_{Cu}$** = 6.11 g$_{Cu}$/g$_{cat}$; **m$_{cat}$** = 0.556 g$_{cat}$.

Experiment 13_6 data

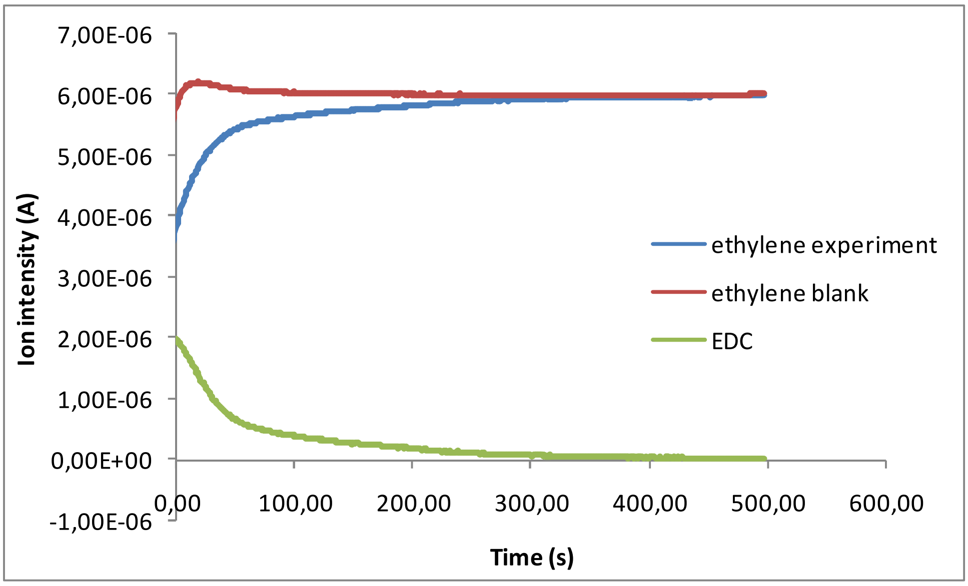

Figure C.63 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **P**$\mathbf{C_2H_4}$ = 0.1 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.556 g_{cat}.

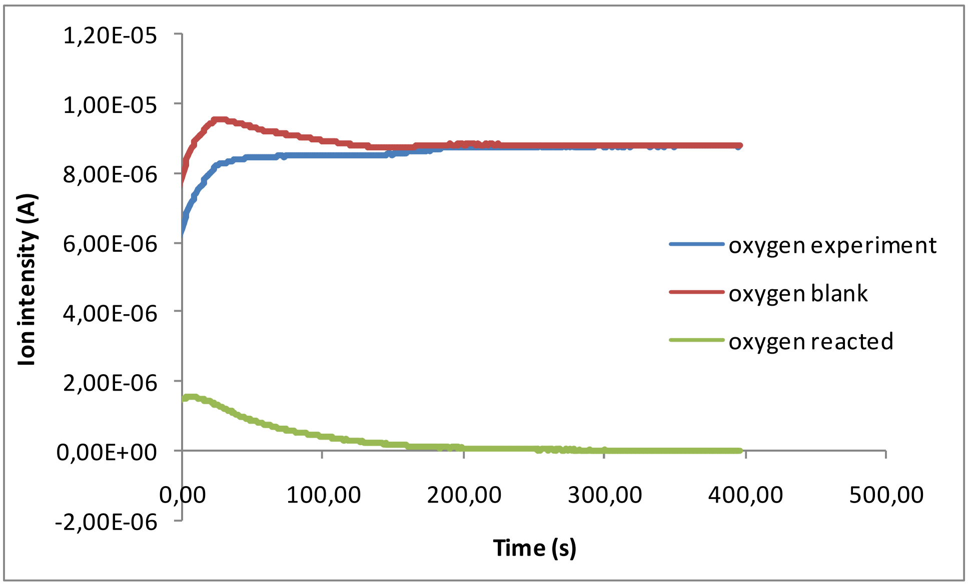

Figure C.64 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **P**$\mathbf{O_2}$ = 0.223 atm; **T** = 493K; $\mathbf{w_{Cu}}$ = 6.11 g_{Cu}/g_{cat}; $\mathbf{m_{cat}}$ = 0.556 g_{cat}.

Experiment 13_7 data

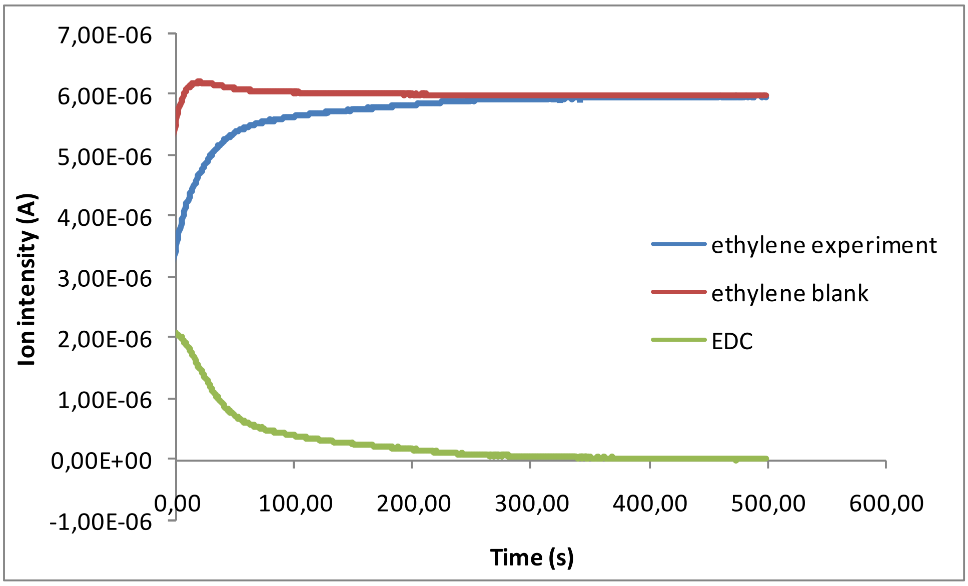

Figure C.65 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

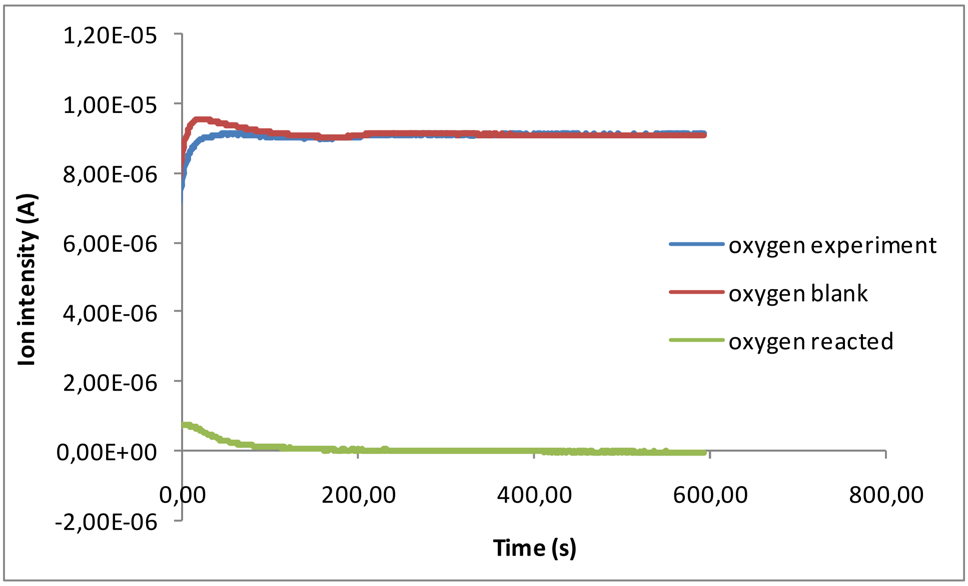

Figure C.66 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 493K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.556 g_{cat}.

Experiment 14_2 data

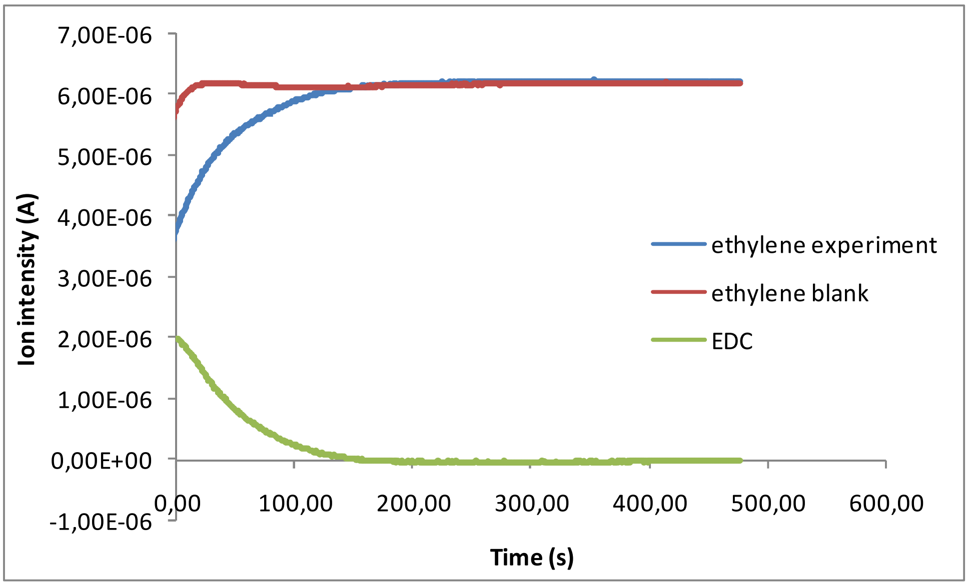

Figure C.67 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

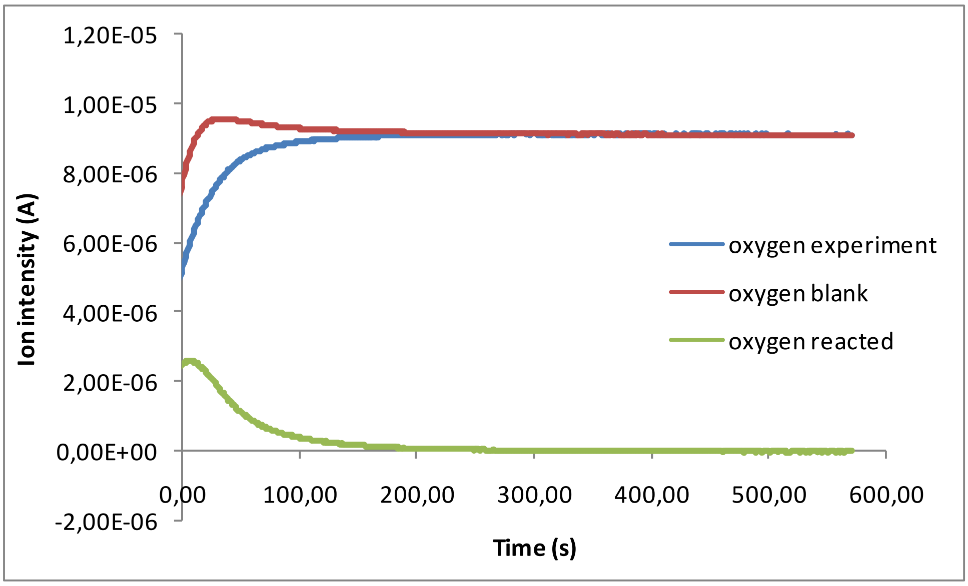

Figure C.68 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 14_3 data

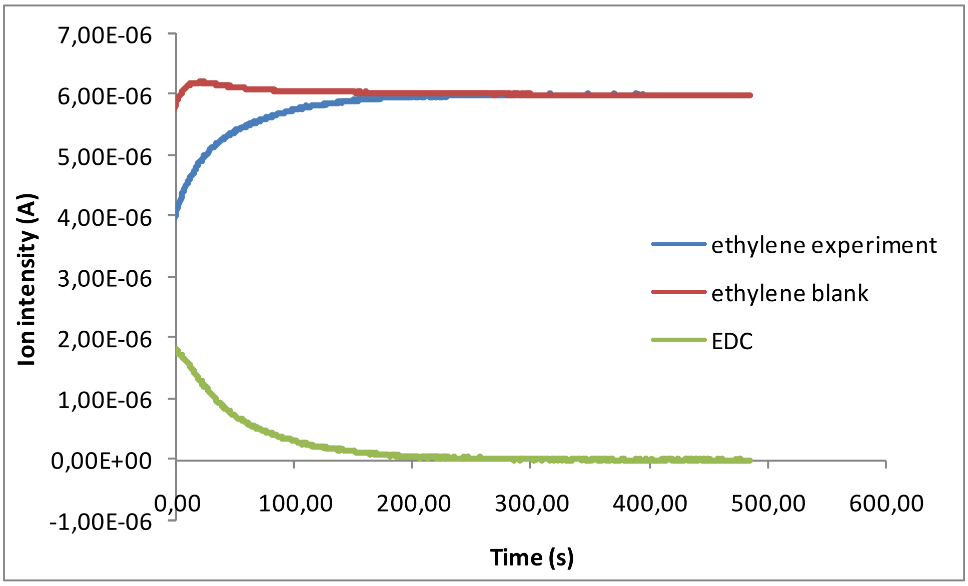

Figure C.69 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.787 ml/s; **PC_2H_4** = 0.085 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

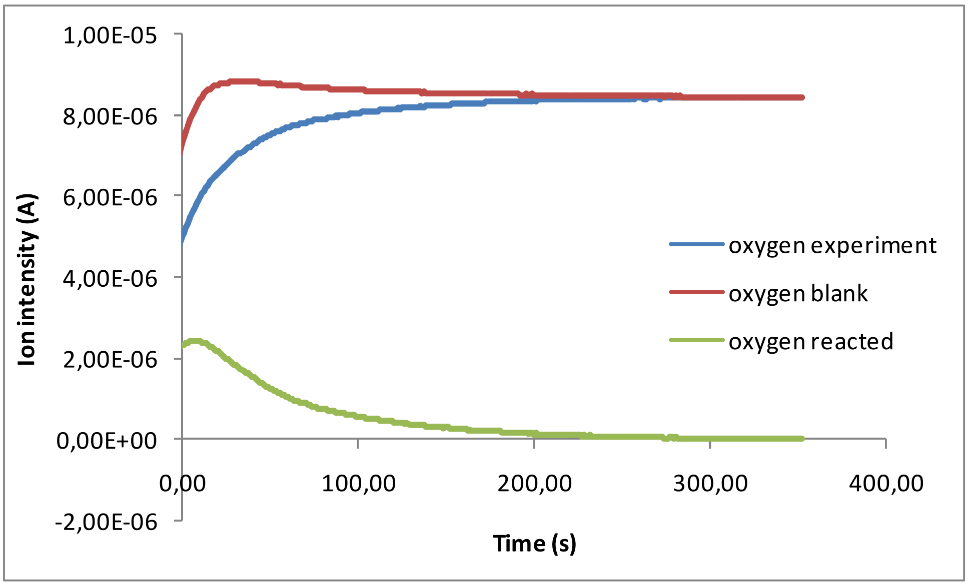

Figure C.70 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.04 ml/s; **PO_2** = 0.223 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 14_4 data

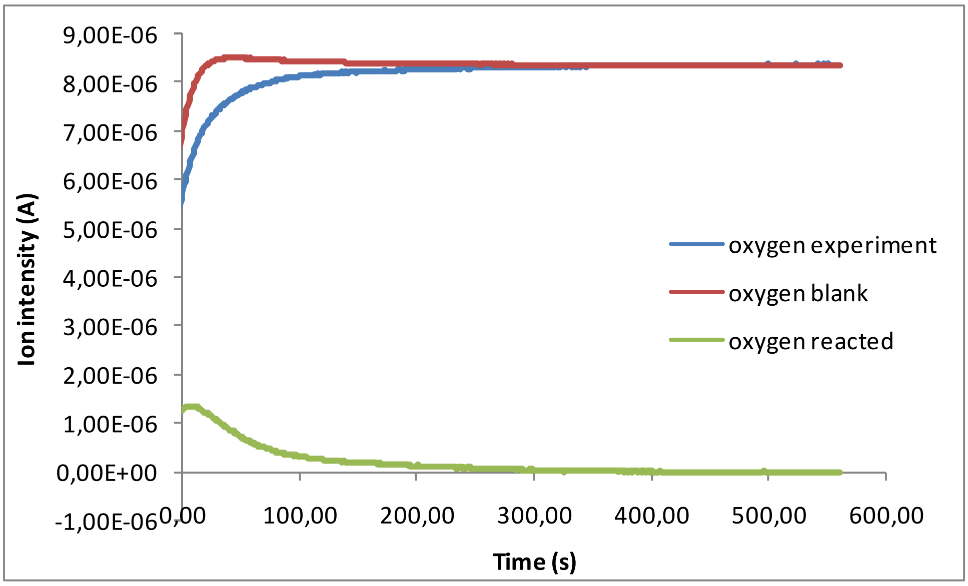

Figure C.71 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; **PO_2** = 0.177 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 14_5 data

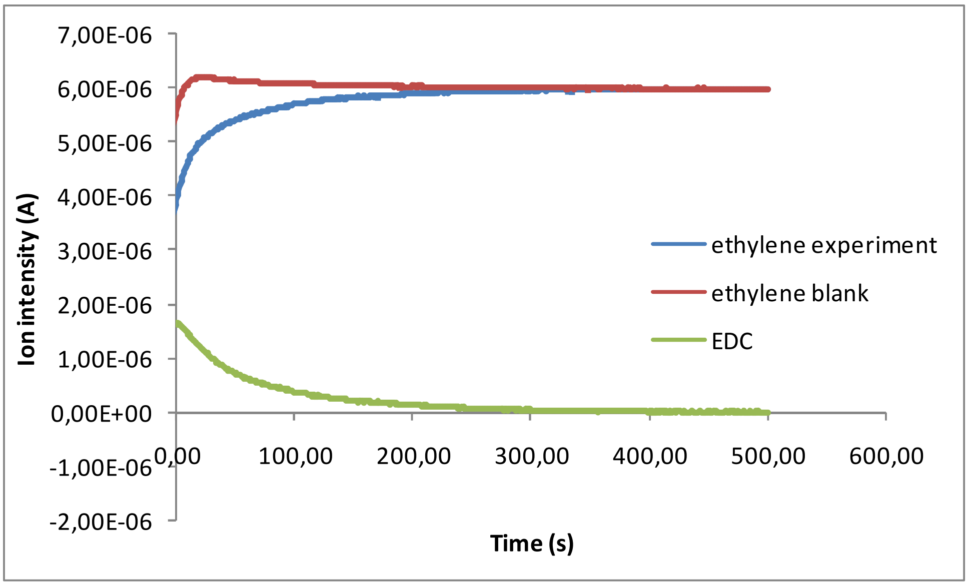

Figure C.72 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.337 ml/s; **PC_2H_4** = 0.065 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

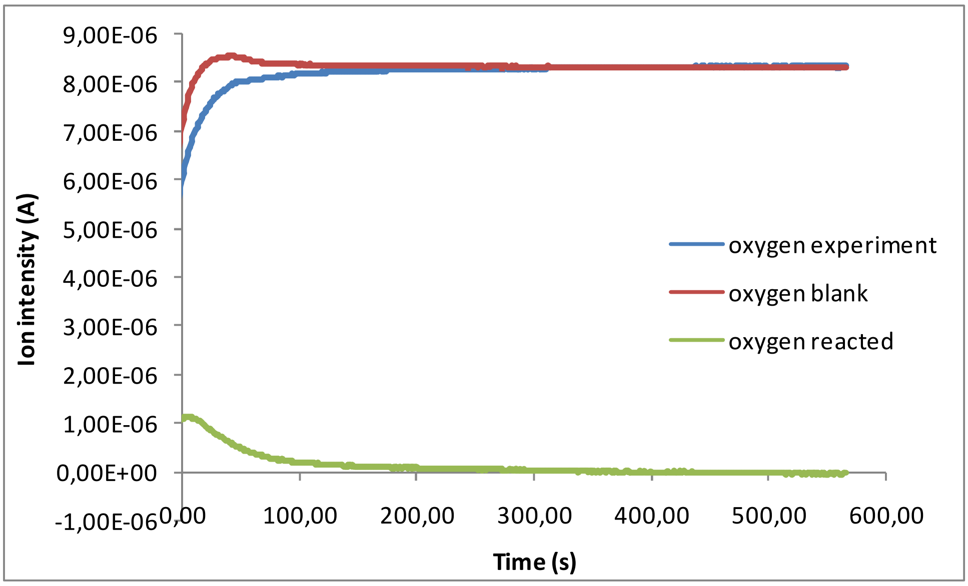

Figure C.73 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.58 ml/s; **PO_2** = 0.147 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 14_6 data

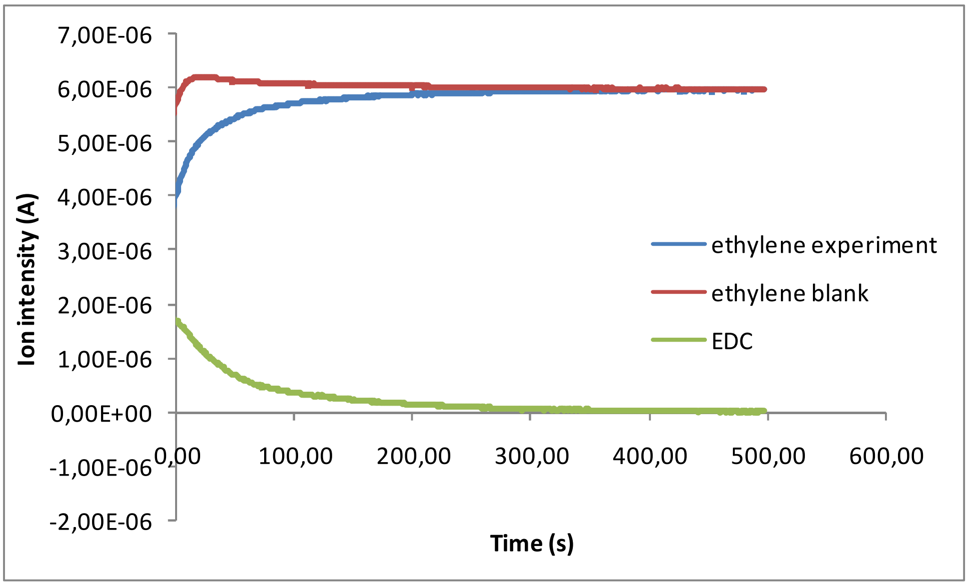

Figure C.74 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.062 ml/s; **PC_2H_4** = 0.073 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

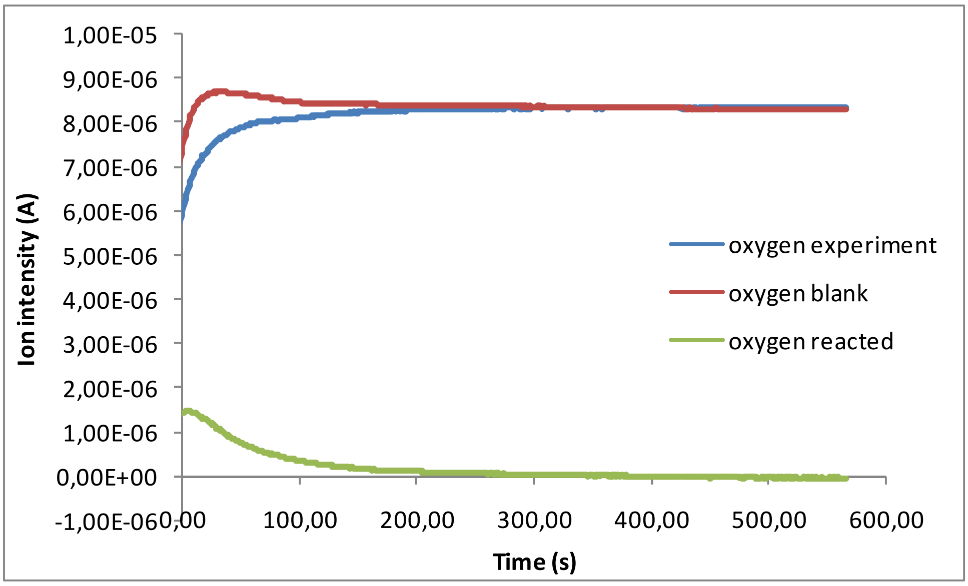

Figure C.75 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 1.31 ml/s; **PO_2** = 0.177 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 14_7 data

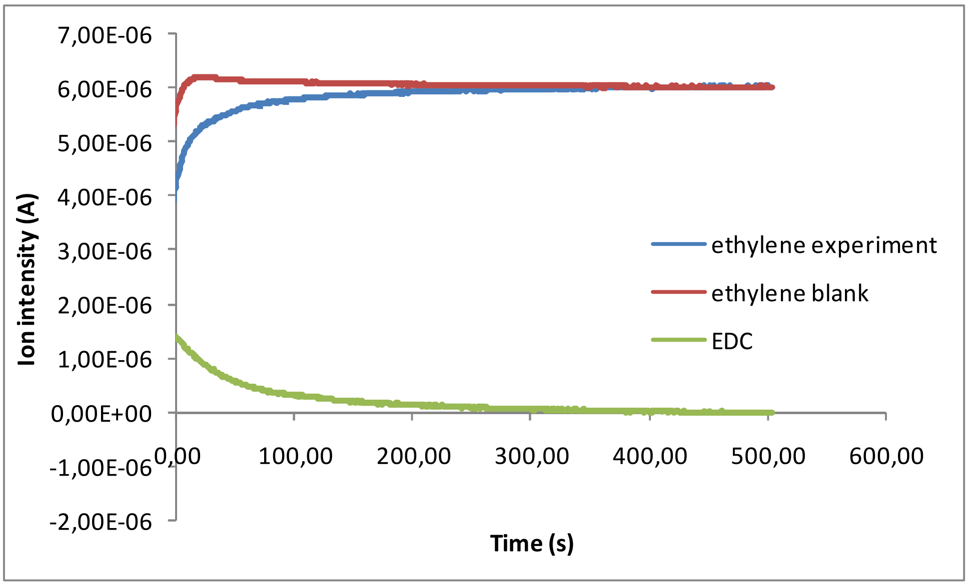

Figure C.76 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 2.612 ml/s; **PC_2H_4** = 0.058 atm; **T** = 483K; **w_{Cu}** = 6.11 g_{Cu}/g_{cat}; **m_{cat}** = 0.523 g_{cat}.

Experiment 18_1 data

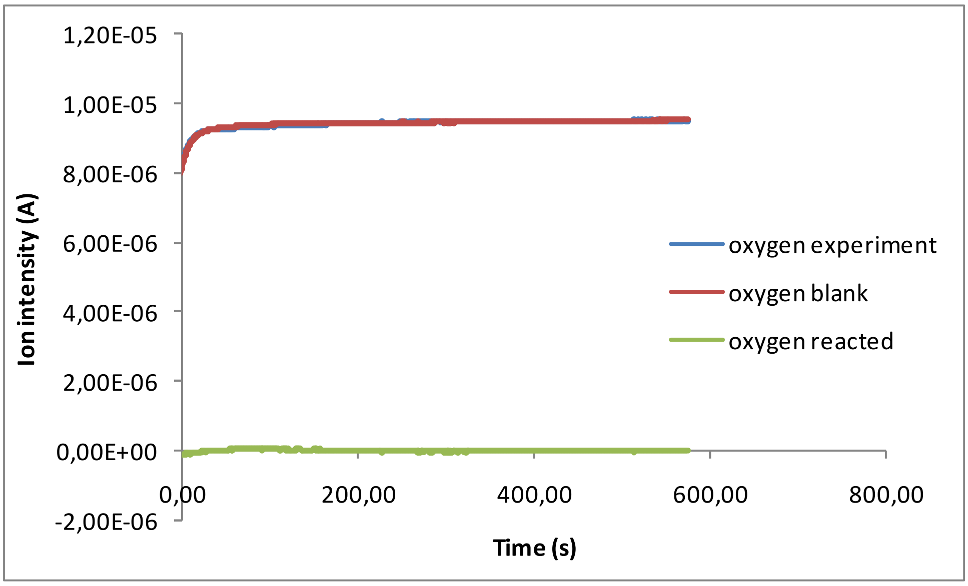

Figure C.77 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO$_2$** = 0.301 atm; **T** = 523K; **w$_{Cu}$** = 3.82 g$_{Cu}$/g$_{cat}$; **m$_{cat}$** = 0.335 g$_{cat}$.

Experiment 18_2 data

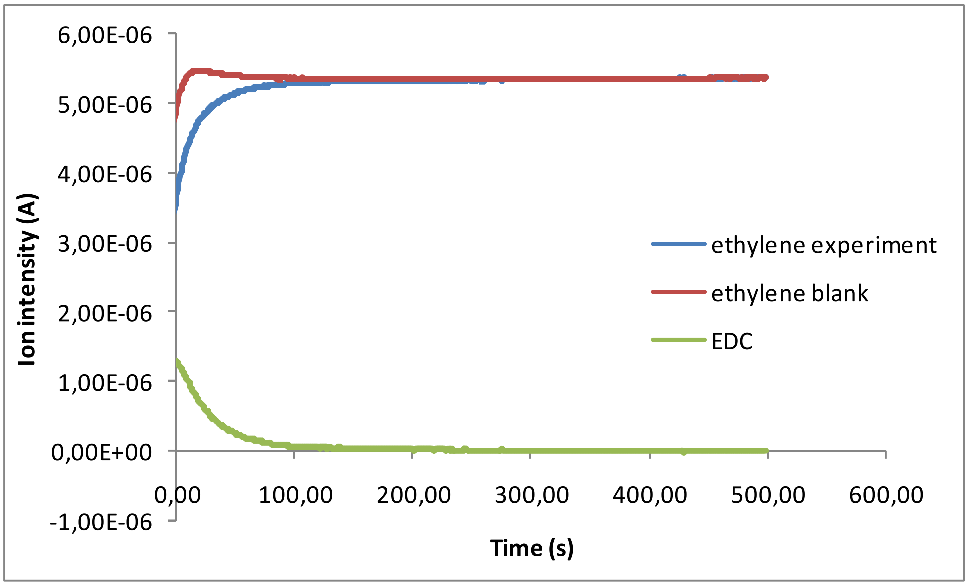

Figure C.78 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.335 g_{cat}.

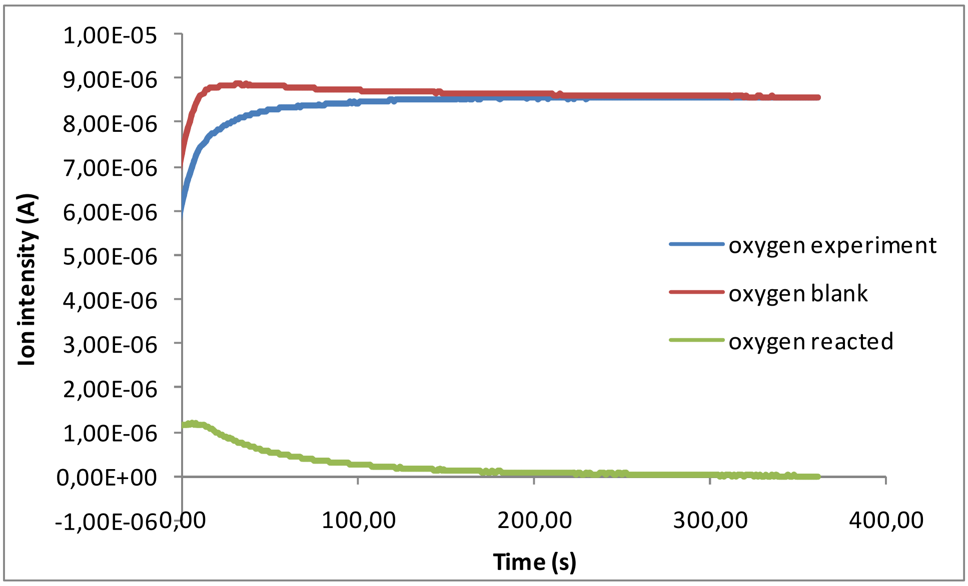

Figure C.79 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.335 g_{cat}.

Experiment 18_3 data

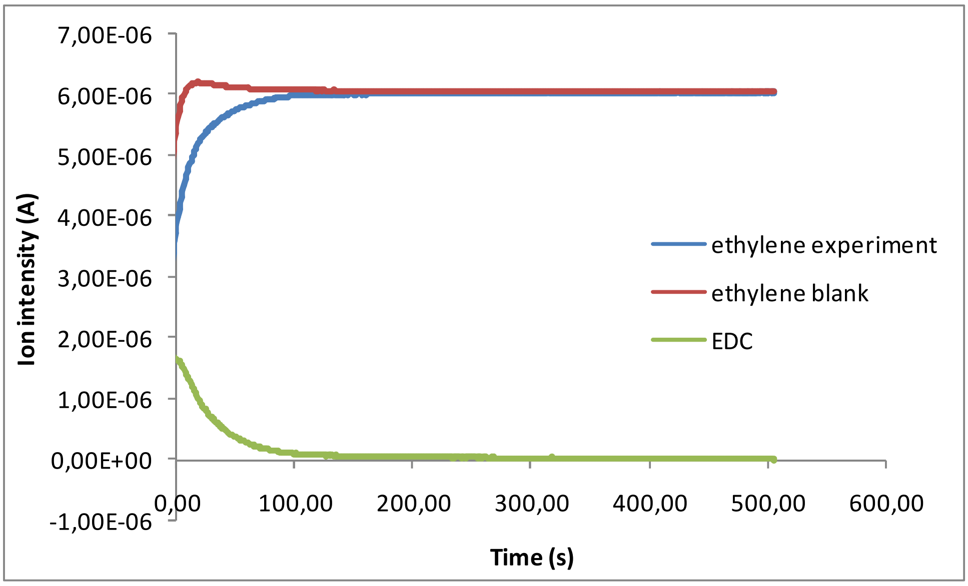

Figure C.80 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.335 g_{cat}.

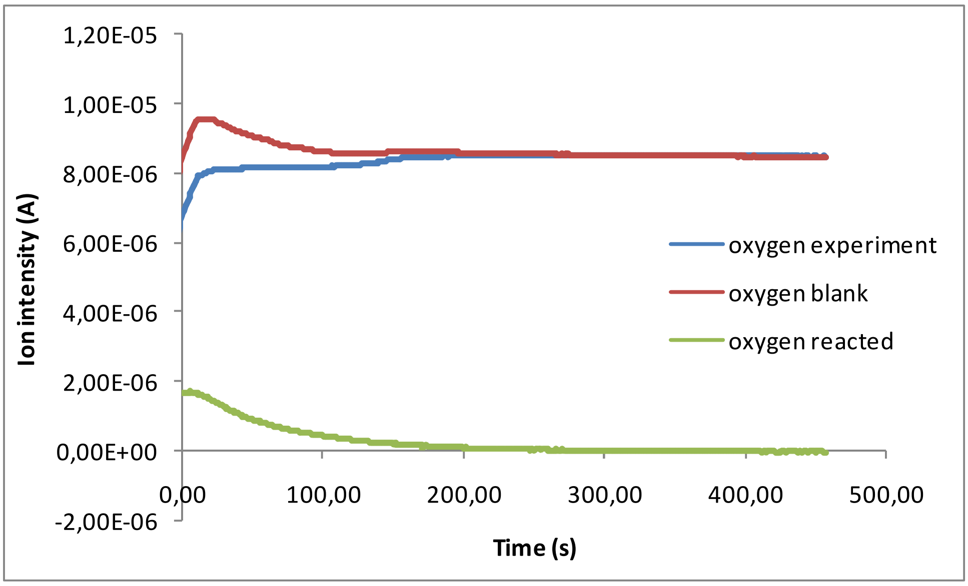

Figure C.81 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.335 g_{cat}.

Experiment 18_4 data

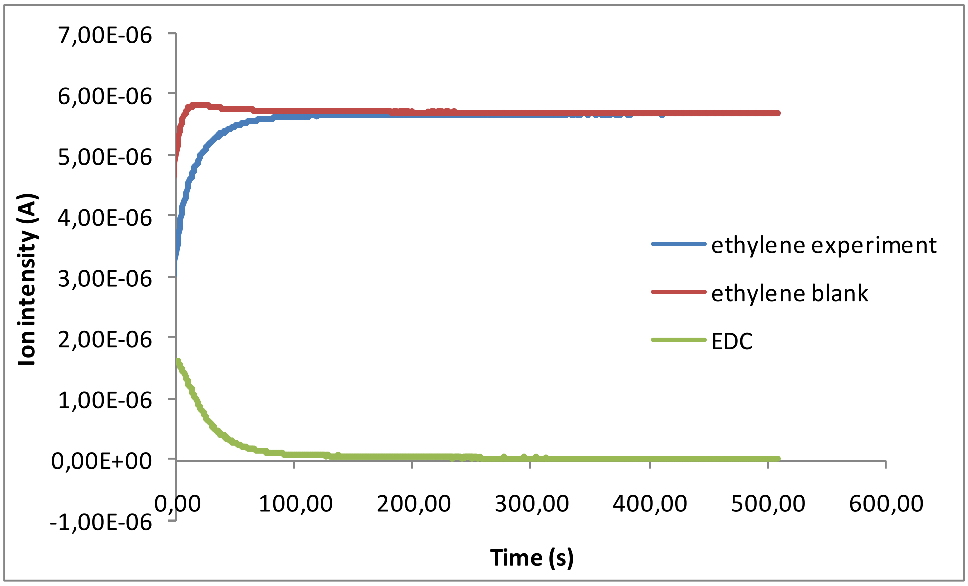

Figure C.82 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w$_{Cu}$** = 3.82 g_{Cu}/g_{cat}; **m$_{cat}$** = 0.335 g_{cat}.

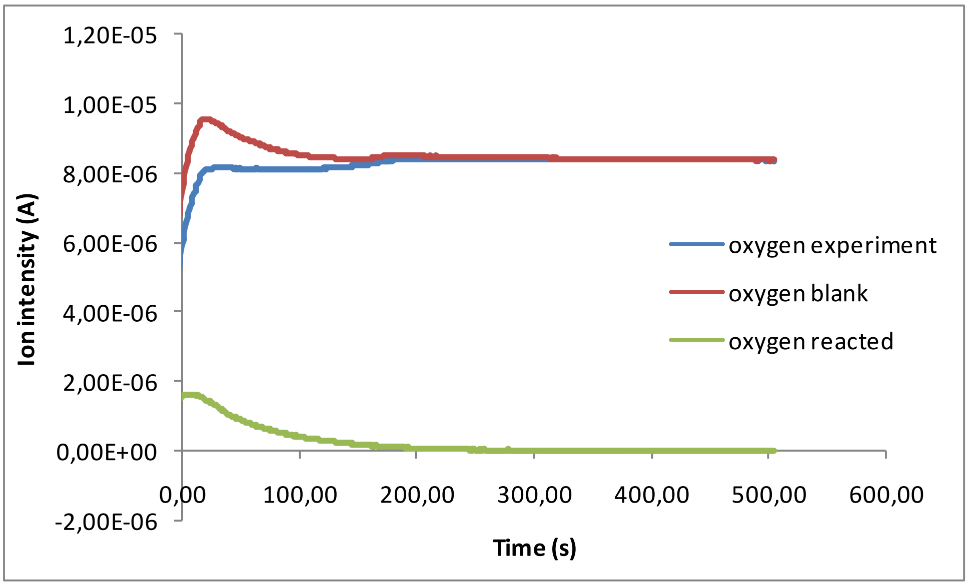

Figure C.83 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w$_{Cu}$** = 3.82 g_{Cu}/g_{cat}; **m$_{cat}$** = 0.335 g_{cat}.

Experiment 18_5 data

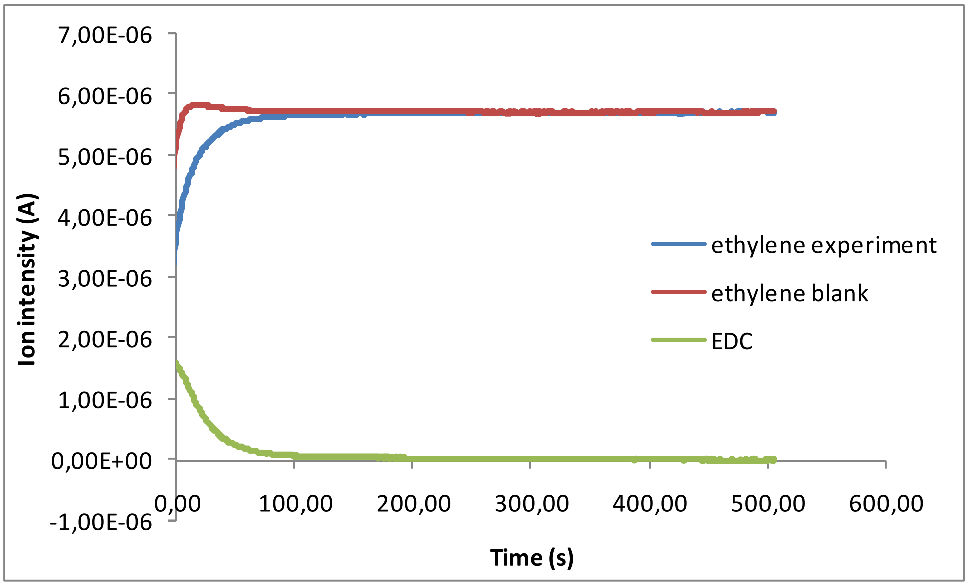

Figure C.84 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.335 g_{cat}.

Experiment 19_1 data

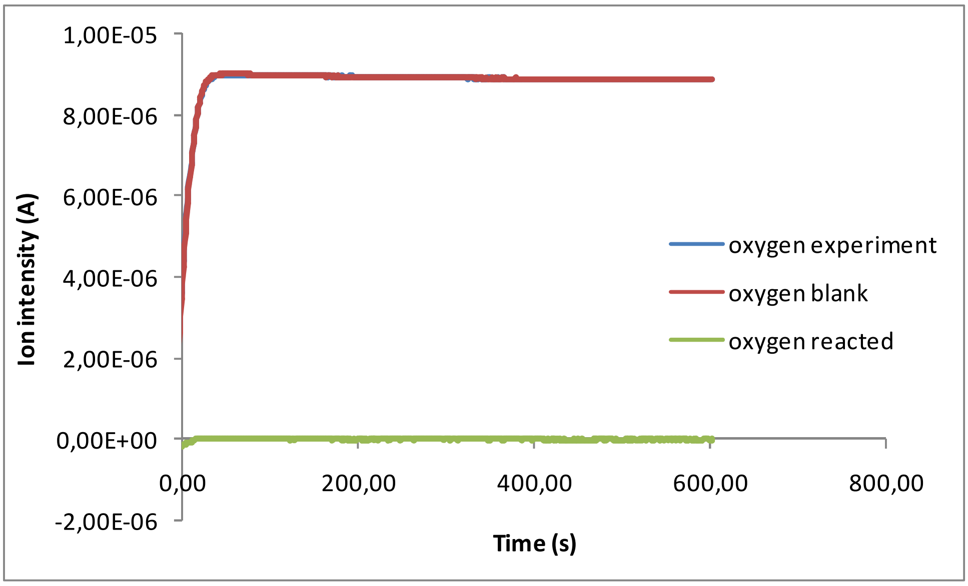

Figure C.85 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

Experiment 19_2 data

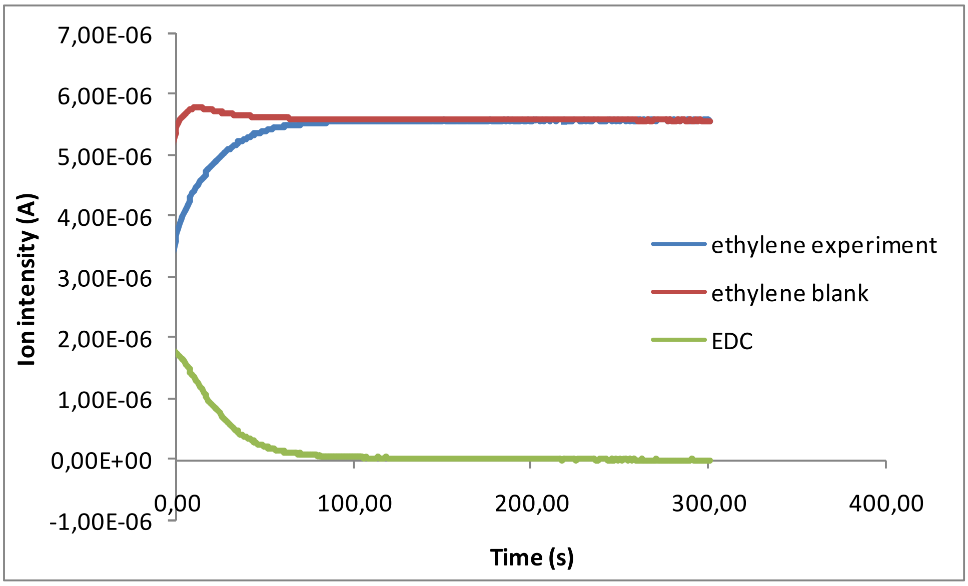

Figure C.86 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

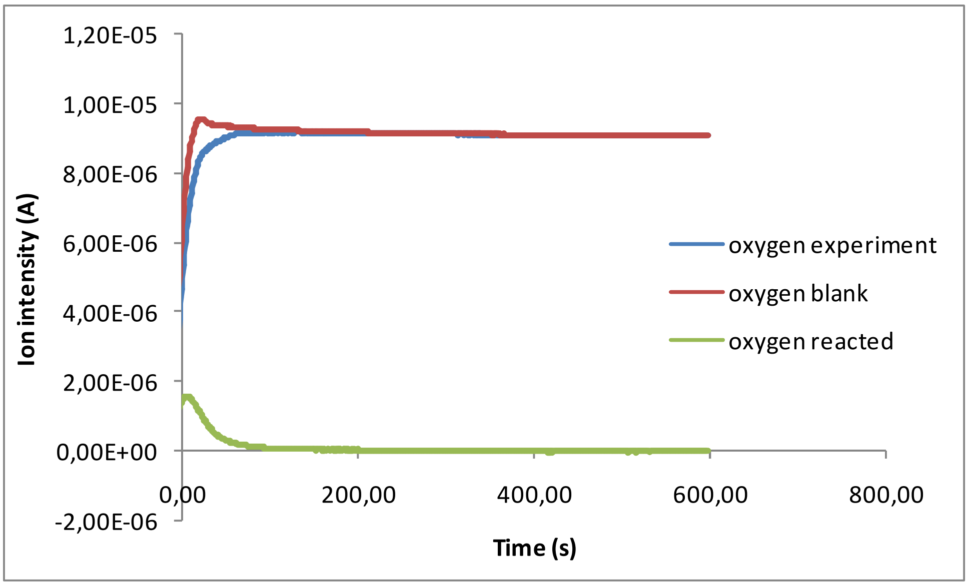

Figure C.87 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

Experiment 19_3 data

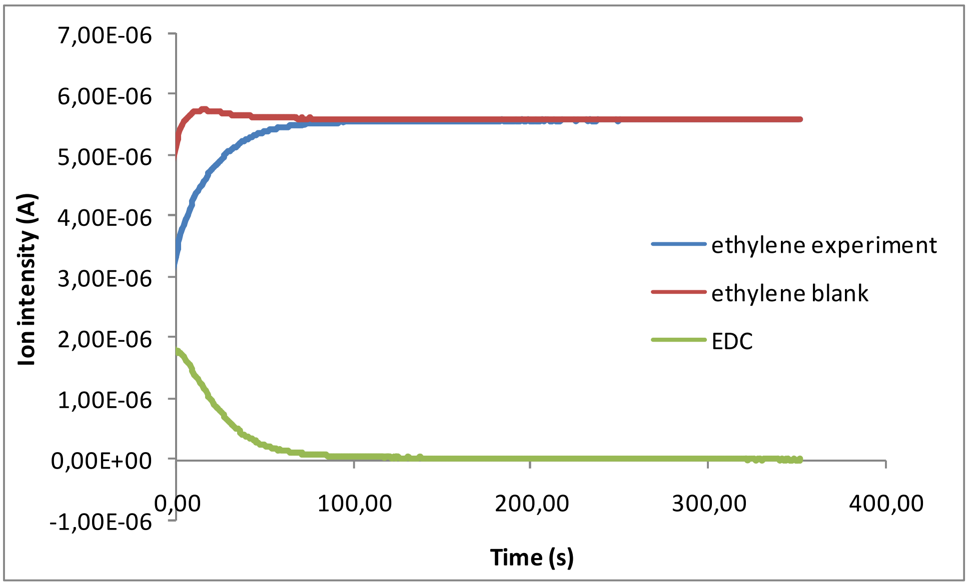

Figure C.88 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

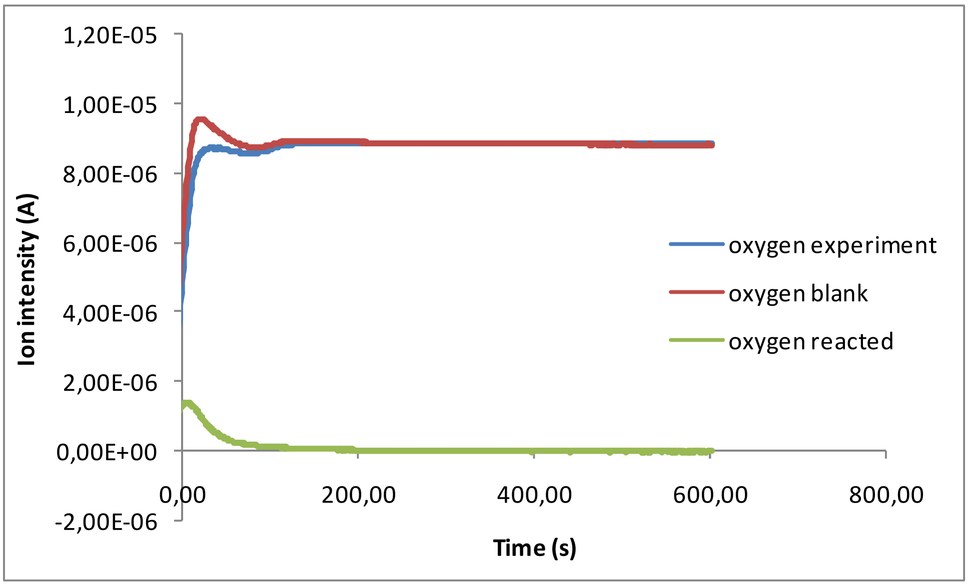

Figure C.89 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

Experiment 19_4 data

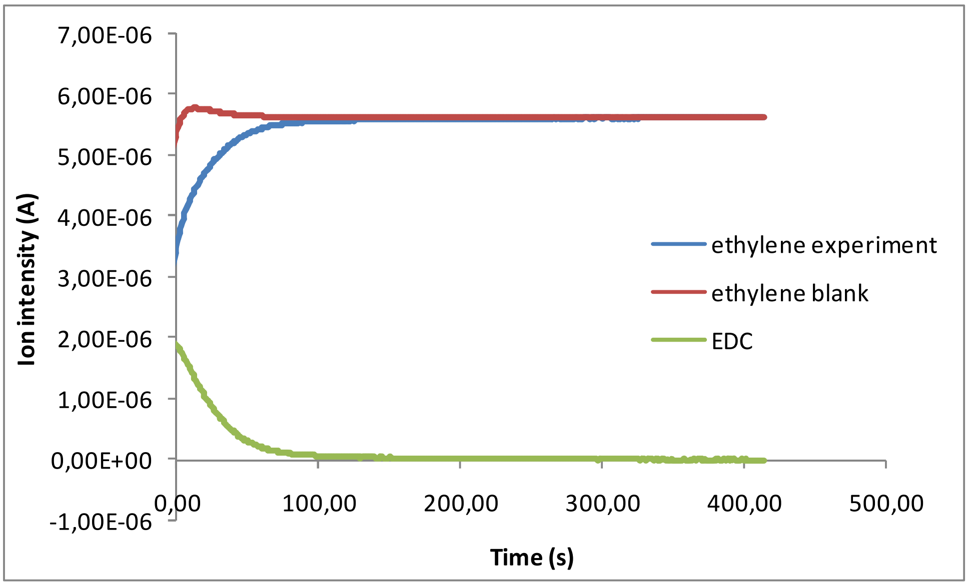

Figure C.90 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

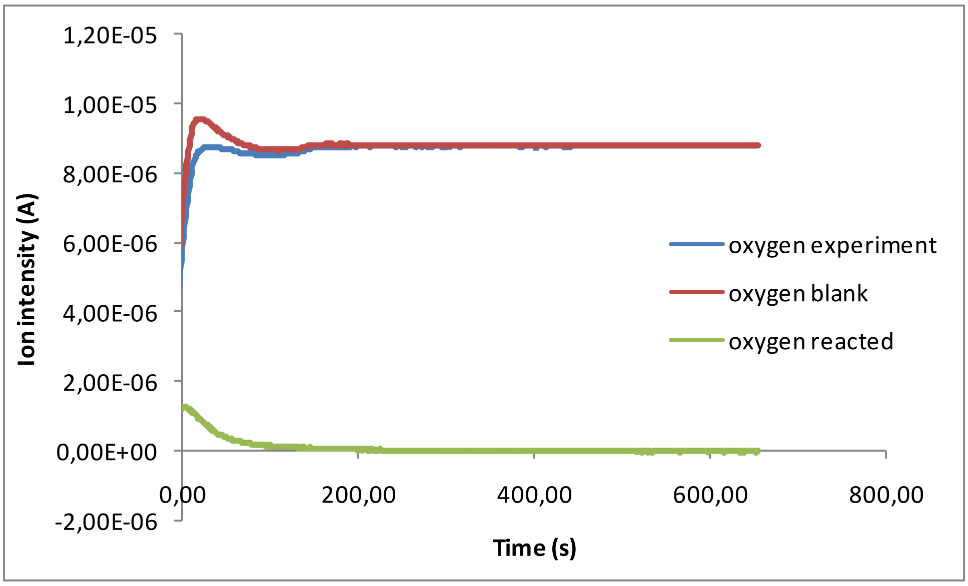

Figure C.91 Experimental data from the second reaction step. Experimental conditions: **Total flow** = 0.77 ml/s; **PO_2** = 0.301 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.

Experiment 19_5 data

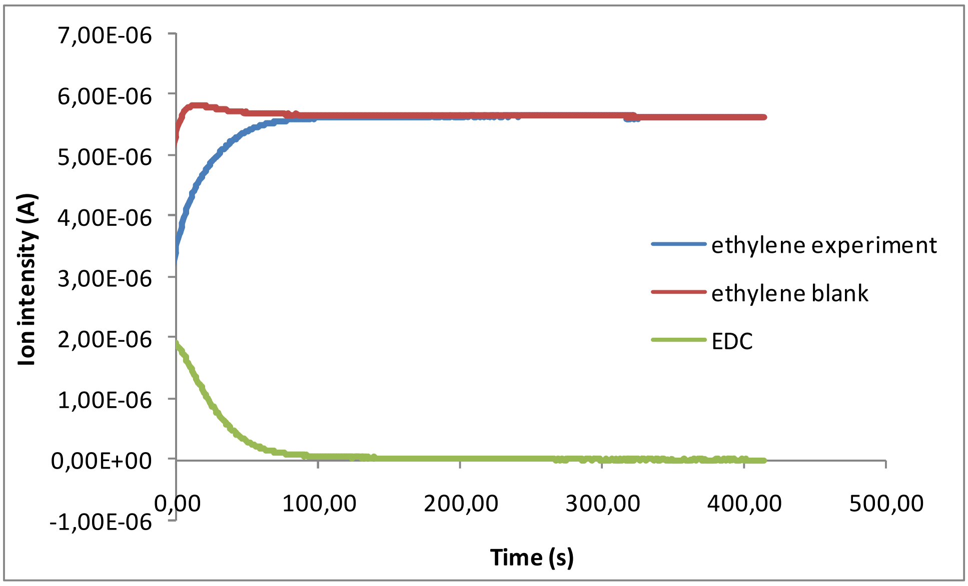

Figure C.92 Experimental data from the first reaction step. Experimental conditions: **Total flow** = 1.512 ml/s; **PC_2H_4** = 0.1 atm; **T** = 523K; **w_{Cu}** = 3.82 g_{Cu}/g_{cat}; **m_{cat}** = 0.360 g_{cat}.