KINETIC STUDY OF OXYCHLORINATION OF ETHYLENE ON COPPER CHLORIDE AND CERIUM OXIDE CATALYSTS

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ABSTRACT

Dichloroethane and vinyl chloride are two very useful components in the industry. Those components are used such as solvents or precursors in the case of dichloroethane, and as monomers to produce polymers, in the case of vinyl chloride, PVC. PVC is a useful polymer, used in almost all the applications developed from the human being, such as construction, medicine, feed industry, etc.

Several works have been made to produce these compounds. In these works, several catalyst have been tried, such as gold and copper in the case of Juszczyk et al.[1] to produce vinyl chloride via dehydrochlorination of dichloroethane, obtaining a vinyl chloride selectivity between 60 and 85 % in case of copper and showing a more propensity to form ethene in case of gold. Other authors, such as Magistro et al.[2] developed a method to produce vinyl chloride directly from ethylene using as catalyst iron oxide.

In this work, the main objective is to obtain the differences between both catalysts and try to develop a reliable model and compare the main reaction products in the oxychlorination of ethylene using two different catalystus. $CuCl_2/\gamma\text{-}Al_2O_3$, catalyst which main reaction product is dichloroethane, $CuCl_2$/CeO2, catalyst which main reaction product was ethyl chloride and cerium oxide, catalyst that according to the results of Scharfe et al.[3] vinyl chloride is the main reaction product. In the case of cupper chloride, conversions between 5-19 % were achieved with a selectivity of dichloroethane around 90 % and no vinyl chloride was observed. A side product observed during these reactions was ethyl chloride. In the case of cerium oxide, vinyl chloride and 1,2 dichloroethane were the main products obtained, alongside with ethyl chloride and carbon dioxide.

1. INTRODUCTION

1,2 Dichloroethane is a colorless liquid with an odor similar to chloroform[4]. The most common use of the compound is the obtaining of vinyl chloride to produce PVC for several industrial applications. Other uses of this compound are the use as a solvent, forming azeotropes with many compounds, including water and butanol[5], and as an intermediate in many organic reactions. This compound was first synthetized in 1794 by Jan Rudolph Deiman and Nicolaas Bondt using ethylene and chlorine.

There are many ways to produce 1,2 dichloroethane, for example in the United States there are two main ways, using two types of catalyst mainly, iron chloride[6] and cupper chloride[7], following the next reactions:

For the case of Iron chloride:

$$H_2C = CH_2 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$$

And for the case of cupper chloride the reaction is the following one:

$$2\,H_2C = CH_2 + 4\,HCl + O_2 \rightarrow 2\,ClCH_2 - CH_2Cl + 2\,H_2O$$

The preferred reaction is the reaction where the catalyst is $CuCl_2$. The main explanation are the reagents used and the temperature needed. In the case of iron catalyst, chlorine is used. Chlorine compared to hydrogen chloride and oxygen, is an expensive reagent, the hydrogen chloride is a side product of many industrial processes and the oxygen can be obtained from the air, nut chlorine must be formed and purified, increasing its value. There is one of the reasons the second reaction is preferred. The second reason is that in the case of iron oxide higher temperatures must be reached.

Vinyl chloride is a gas phase compound colorless and unstable at high temperatures. It was first synthetized by 1835 by Justus von Liebig[8]. He obtained this compound by treating the 1,2 dichloroethane with a solution of potassium hydroxide in ethanol. Later, in 1912 Fritz Klatte patented a method to produce this compound using acetylene and hydrogen chloride, using mercury chloride as catalyst. The main problem with this synthesis is the mercury, due to the high risk for the health and the environment that it takes[9], so this way of production is nowadays not used anymore.

The main ways to produce vinyl chloride are basically:

- Direct hydrochlorination of acetylene using metallic compounds as catalysts[10,11]:

$$C_2H_2 + HCl \rightarrow H_2C = CHCl$$

- Thermal cracking of 1,2-dichloroethane[12,13]:

$$ClCH_2 - CH_2Cl \overset{\Delta}{\rightarrow} H_2C = CHCl + HCl$$

- Production from ethylene, using three different ways:

  1. High temperature chlorination:

$$C_2H_6 + 2\,Cl_2 \rightarrow C_2H_3Cl + 3\,HCl$$

  2. High temperature oxychlorination

$$C_2H_6 + HCl + O_2 \rightarrow C_2H_3Cl + 2\,H_2O$$

  3. High temperature oxidative chlorination

$$2\,C_2H_4 + Cl_2 + \frac{1}{2}\,O_2 \rightarrow 2\,C_2H_3Cl + H_2O$$

Now, the preferred way to produce vinyl chloride is from 1,2-dichloroethane. Most of the factories producing this monomer go with this technique, it is the cheapest one because it only need heat to dehydrochlorinate the 1,2 dichloroethane.

Nowadays, the production of vinyl chloride is very high. There are projects running of plants which prevent to produce 29000 tons per year[14]. These processes are usually attached to processes of production of dichloroethane, due to the production of vinyl chloride from this product is quite easy.

The main trouble with vinyl chloride is its hazardous risk it can present on human health. As well as it polymer does not present, vinyl chloride has a proved hepatoxicity[15] since 1930. It can also have negative effects in the skin, lungs and eyes[16]. That is the main reason, why almost every plant nowadays run these processes with the minimum people possible.

In this work the main objective is to understand the differences between the catalysts and try to develop a reliable model for everyone of them.

According to Vajglova et al.[17], cupper chloride is a nice catalyst to produce dichloroethane. Using temperatures between 200 and 250 ºC, around 15-16% of conversion can be reached of ethylene into dichloroethane with a selectivity of 90 %. Furthermore, in her work, she studied the influence of the support as an important factor to maximize the production of dichloroethane. In this work, the $CuCl_2/\gamma\text{-}Al_2O_3$ catalyst and way of preparation will be used to recreate the conditions.

According to Scharfe et al.[3], oxychlorination of ethylene can be achieve using ceria as the catalyst. The main product in their work were vinyl chloride and 1,2 dichloroethane. The temperatures in this case are much higher, reaching the 450 ºC to begin the reaction of the ethylene into vinyl chloride. Conversion of ethylene reached the 50 % and the selectivity of vinyl chloride was around 25 %.

In this work to understand the differences with the catalysts and try to develop a model of the behavior of the chlorination of ethene, several catalysts will be used: cupper chloride supported over γ-alumina, cupper chloride supported over cerium oxide and cerium oxide catalyst. Different temperatures were studied to see its influence in the reaction rates and selectivity. Different ratios of inlet flow were studied to see the influence of the ratio of the different components during the oxychlorination reaction, such as hydrogen chloride and oxygen.

2. EXPERIMENTAL

2.1 MATERIALS

The materials used for this work are the following ones. For the catalyst, $CuCl_2 \cdot 2\ H_2O$ (CAS Nº: 7447-39-4, provided by Honeywell®), $\gamma\text{-}Al_2O_3$ (CAS Nº: 1344-28-1, provided by UOP®) and in the case of cerium catalyst $Ce(NO_3)_3 \cdot 6H_2O$ (CAS Nº:10294-41-4, provided by Sigma Aldrich®), NH4OH 32% (CAS Nº:, provided by Sigma Aldrich®).
For the reaction N_2 (CAS Nº: 7727-37-9, provided by OY AGA Ab), O_2 diluted in He 20% (CAS Nº: 7782-44-7, provided by OY AGA Ab), C_2H_6 (CAS Nº: 74-85-1, provided by OY AGA Ab), HCl 99.99% purity (CAS Nº: 7647-01-0, provided by OY AGA Ab) and glass beads size between 425 - 600 µm provided by Sigma Aldrich®. Filter paper with ⌀ pore of 7-14 µm provided by Whatman®

2.1.1 CATALYST PREPARATION

CUPPER BASED CATALYST

In the case of the cupper-based catalyst with the nominal loading of 5 % wt. The catalyst was prepared from a suspension 250 mL of 0.02 M aqueous solution of the metal precursor and 5 g of the catalyst support. The pH was checked after the suspension was formed. The suspension was stirred during 24 h at 50 ºC in a rotavapor equipment. After the time is over, the suspension was evaporated using a rotavapor equipment at low pressure and 40 ºC, obtaining the alumina coated with $CuCl_2$ particles. After the coating of the catalyst is over then it is dried in an oven at 100 ºC during at least 7 hours. After the drying, the sample is calcinated using an oven provided by Nabertherm® using the following configuration:

Heating: 70 minutes until 250 ºC is reached. The temperature keeps constant during 50 min at 250 ºC. The sample is heated until 450 ºC for 45 minutes, the calcination temperature. The calcination step is kept for 180 minutes. Then the oven is cooled until room temperature.

After the calcination step the sample was stored for further use and analysis. The final sample can be observed in Fig.1 on the left.

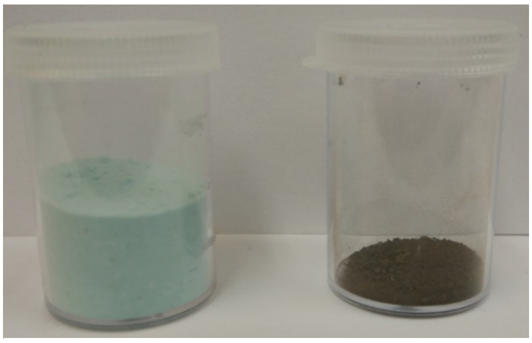


Fig. 1 Comparison between the catalyst supported over alumina (left) and cerium oxide (right)

A copper-based catalyst was also prepared, but instead of alumina, cerium oxide was used as support. The cupper chloride was deposed over the cerium oxide using the evaporation-impregnation method. First a solution of 5 % wt of copper was prepared using copper chloride (II). After this a suspension was formed using the cerium oxide in a concentration of 0.12 M of cerium oxide. This suspension was heated and rotated during 24 h at a temperature of 60 ºC using a rotavapor equipment. After this, the catalyst was dried in a rotavapor. Then it was kept in an oven at 100 ºC during at least 7 hours to evaporate all the moisture that can remain in the catalyst. After the drying it was calcinated using the same procedure as in the case of the copper over alumina catalyst.

After this the catalyst was stored for further use and analysis. The final catalysts can be observed in Fig. 1 as well on the right.

CERIUM CATALYST

According to the results of Leino et al.[18], obtaining particles of CeO_2 and surfaces between 110-120 m^2/g, the cerium catalyst was prepared using the method proposed by the last author cited. First a diluted solution of $Ce(NO_3)_3 \cdot 6H_2O$ was prepared. After that, the pH of this solution was adjusted adding drop by drop to a precipitating base solution prepared with NH_4OH 32% solution until the pH 11 was reached. The mixture was stirred at a constant speed of 150 rpm and the pH was controlled at constant periods of time for 5 days. During this time, it could be observed several changes of color of the solution. First the cerium solution was transparent. After adding it to the precipitating solution, the color changed to red, showing the formation of $Ce(OH)_3$, and after one day approximately, the color changed to yellow, the color of the CeO_2, the interest compound. These color changes were also reported by Leino et al[18]. in their work.

After the synthesis period, the mixture was filter using a Büchner-kitasatos equipment. The catalyst in the filter was then dried at ambient conditions. The remained suspension in the kitasatos was evaporated using a rotavapor equipment, obtaining in the vessel the CeO_2 that the filter could not retain.

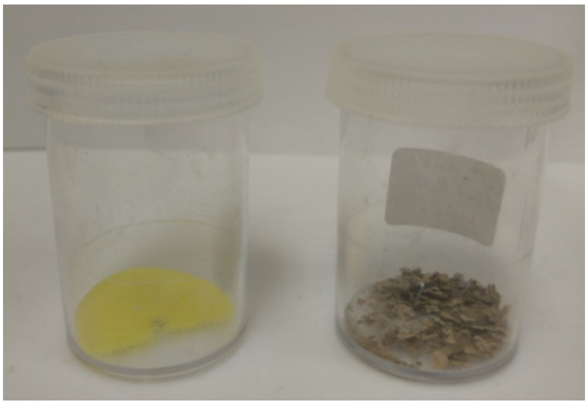


Fig. 2 Comparison between the cerium oxide obtained by filtration (left) and the one obtained by evaporation (right)

After the catalyst was synthetized it was calcinated using the same procedure that in the case of cupper-based catalyst. It was observed that the catalyst obtained using the rotavapor equipment did not resist the conditions of calcination, sintering and acquiring a texture and color like the burnt paper.

After the calcination, the catalyst was stored for further use and analysis.

2.2 ANALITICAL METHODS

2.2.1 CATALYST CHARATERIZATION

COPPER BASE CATALYST

The analytical methods used to analyze the copper based catalyst, such as nitrogen physorption, Fourier transform infrared spectroscopy, Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX), Transmission electron microscopy, Temperature programme desorption (TPD) of CO_2 and X-Ray powder diffraction, were the same as used in the work of Vajglová et al.[17], as the same catalyst with the same catalyst preparation was used.

CERIUM OXIDE CATALYST

The analytical methods used to analyze the cerium oxide catalyst, such as X-ray diffraction, Transmission electron microscopy, Cluster size distribution and specific surface area, Acidity and basicity of the catalyst and X-ray electron spectroscopy (XPS), were the same as the ones used in the work of Leino et al.[18], as the same way catalyst preparation was used.

2.2.2 REACTION PRODUCTS

The reaction products are analyzed using a gas chromatographer provided by Agilent Technologies. The components out of the chromatographer are analyzed in a TCD and FID detector. The samples for the analysis are taken periodically in a time interval of 65 minutes.

2.3 REACTION

TUBULAR REACTOR

For the reaction in tubular reactor with dimension of 30 cm length and 1 cim inner diameter, heating the apparatus to 120 ºC, the equipment used was a station equipped with 5 gas flowmeters provided by Brooks instruments, version 3.20. The components used for the reaction are C_2H_4 as main reactive, O_2 and HCl, and N_2 to dilute the inlet reaction mixture and as inert standard for GC. The inlet ratios are 30.4 % vol, 2.4 % vol, 9.5 % vol and 57.4 % vol respectively. The flowmeters were calibrated in N_2 base and controlled using the software provided by the same company.

The reactor is heated using an electric furnace, measuring the temperature using the software PicoLog® to assure a constant temperature. The oven and catalyst temperature are measured using thermocouples based in K Ni Cr the cation and K Ni Al the negative part.

After that, the flows are combined in a mixing point and taken to the reactor. In the reactor three stages are differenced. The first stage is the first third part of the reactor, filled only with glass beads, to assure a good mixing of the reaction mixture. After that, the second third part of the reactor is filled with a mixture of the catalyst and glass beads in a range of 3 - 5.6 % of catalyst. The particle size of the catalyst is prepared between 250-500 µm.

Following the reactor, a by-pass is used to remove part of the mixture, to protect the GC of some of the aggressive reagents in the mixture, such as HCl or O2. Then the mixture is lead to the GC where the analysis is taking place. After the analysis is made, the mixture is removed.

3. RESULTS AND DISCUSSION

3.1 EQUILIBRIUM CALCULATIONS

For this reaction, the equilibrium calculations were the first thing done. The equations used for these calculations were the Van't Hoff equation[19] and the definition of free Gibbs energy.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K$$

$$2\ C_2H_4 + Cl_2 + \frac{3}{2}\ O_2\ \rightarrow 2\ C_2H_3Cl + 3\ H_2O$$

Eq. 1 Free Gibbs energy equation, Van't Hoff equation and reaction to which the calculations were made.

The data for the different components, ethylene, hydrogen chloride, 1,2-dichlorethane and water were obtained from NIST Database[20]. The results are presented here:

∆G (250 °C) [J/mol]	∆G (450 °C) [J/mol]	K (250 °C)	K (450 °C)
-82402	-22657	168982284	43.31

As the results show, the equilibrium is hard favorable for the direct reaction. There is almost no reverse reaction, so it can be concluded that the reaction can be treated as irreversible.

3.2 COPPER CHLORIDE SUPPORTED OVER γ-ALUMINA CATALYST

The first experiments done in the cupper chloride catalyst were stability test of the catalyst. These experiments were done to view the stability of cupper chloride catalyst after several days working.

Two types of experiments were carried. One experiment in continuous, several days working, and other experiment in several days but cooling down after every experiment the reactor. This was made to see if the catalyst suffers any deviation after cooling down and been heated again to reaction temperature.

After these experiments, the effect of the temperature was studied. These experiments were carried to develop a model, to find the influence of the temperature in the reaction and calculate the activation energy of the reaction afterwards.

The next experiments were the ones carried out to find the relation of the different concentrations of the reagents to obtain the influence they might have in the reaction order for the model developing. The two reagents studied were the oxygen and the hydrogen chloride. These reagents were changed its concentrations to see if this affects to the reaction and final products.

3.2.1 STABILITY TESTS

The first experiment carried out was the stability test of the cupper chloride over alumina in continuous. This experiment was carried out for 90 hours, using a reagents inlet composition of 30.4% of ethylene, 2.7 % of oxygen and 9.5 % of oxygen, the rest 57.4 % is nitrogen, an inert gas. The amount of catalyst used is 0.5 g of catalyst diluted in 8.5 g of glass beads, with a particle size between 500 and 250 μm. The temperature selected was 225 °C because most of the works done with this catalyst and reaction is around 200 and 300 °C, like the works of Leofanti et al.[21] who studied the mechanism of the reaction of oxychlorination of ethylene using as catalyst copper chloride and Born et al.[22] who studied the oxychlorination reaction using different types of catalyst and reporting the effect of temperature in different copper based catalyst. At higher temperatures the copper sinter and the catalyst is destroyed. The results are presented here:

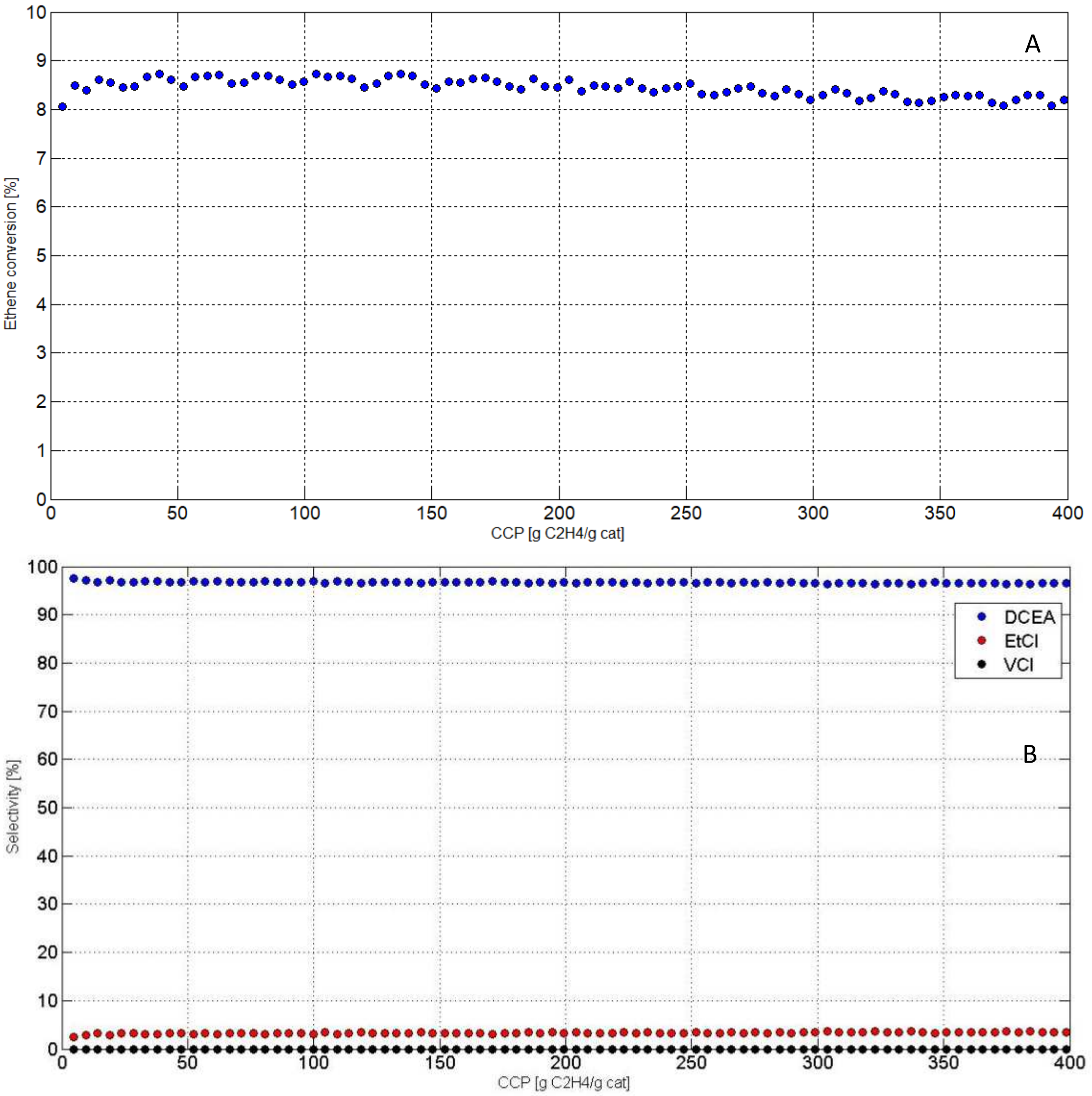


Fig. 3 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B)

Like it can be seen in the results, after this experiment, the cupper chloride catalyst results to be stable after 90 hours. This can be seen in the conversion of the ethylene, showing a very stable conversion, almost not changing with time. Also, a good stability was observed in the selectivity, which remains stable as well during all the working hours, showing a huge tendency to form 1,2-dichloroethane using this catalyst with more than a 95 % of selectivity and only ethyl chloride is observed as a side product, showing that the ethylene is not being oxidized by the oxygen and not turning into CO_2.

In the case of the intermittent experiments, the conditions are the same ones except for the temperature, which was increased until 250 °C. The experiments have a time of 24 h each. The time between them is 24 h as well, meaning that the total time of experiment was 168 h. The results are presented then:

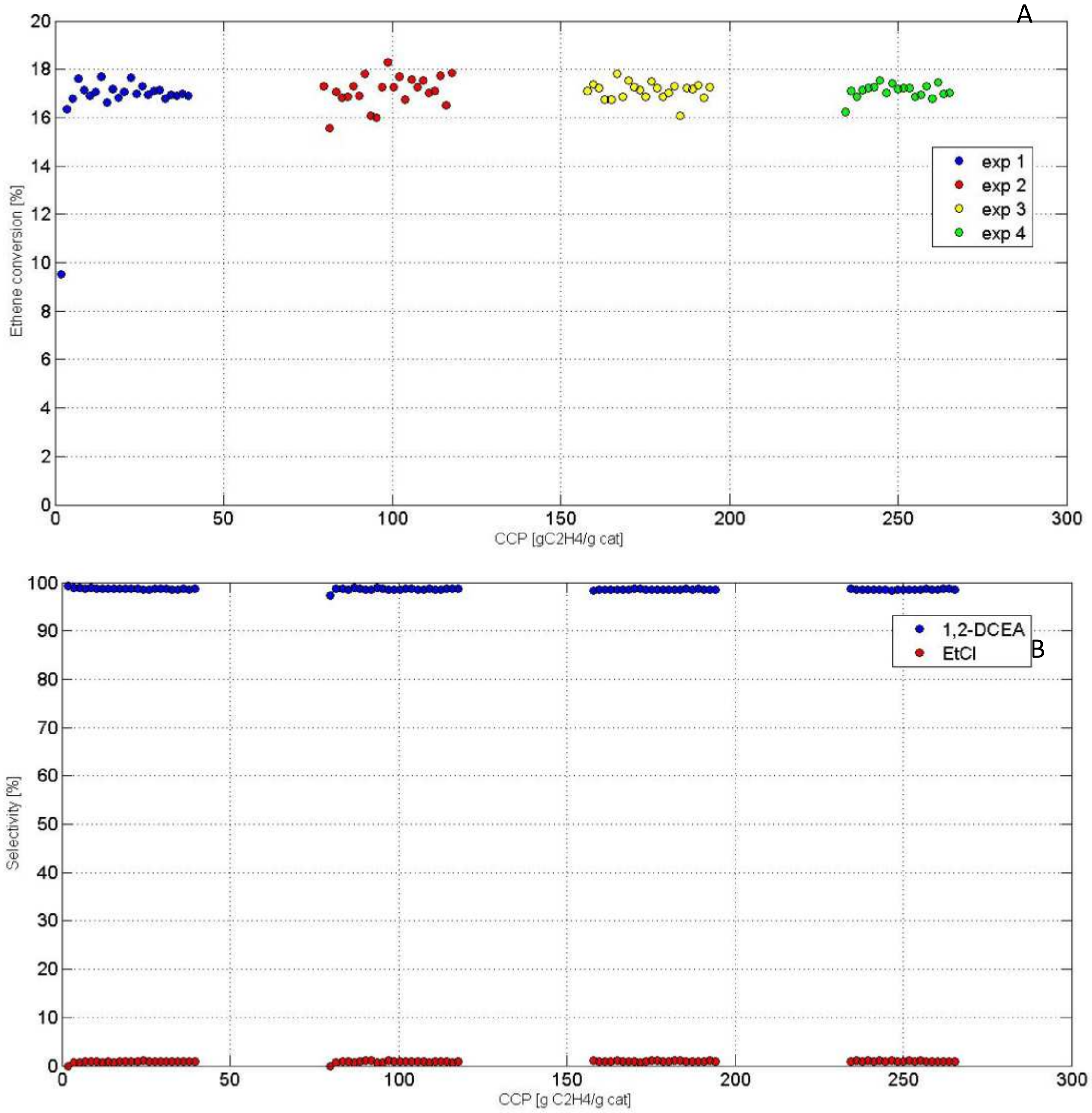


Fig. 4 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B)

These results show a very stable behavior of the catalyst as well. It can be seen in the conversion, the it maintains constant in the same range of values between 16 and 18% after being the catalyst cooled down and heated up for four times. These results show a good thermal stability of the catalyst. The selectivity also maintains constant, being a selectivity higher of 95 % for 1,2-dichloroethane and only ethyl chloride is the side product observed.

With these results, it can be assured that the stability of the catalyst during the experiments can be assured, showing a good stability after many hours working and a good thermal stability after being heated up and cooled down several times.

3.2.2 TEMPERATURE DEPENDECE

For study the temperature dependence, three experiments were carried out. Every experiment was done at different temperatures. The temperatures used for these experiments were 175, 200, 225 and 250 $^{o}C^{21,22}$. These experiments were carried out to develop the model of the reaction and its influence on the reaction rate. The expected results are that the higher the temperature is the higher the conversion of the reagents should be. The results obtained are ºpresented then:

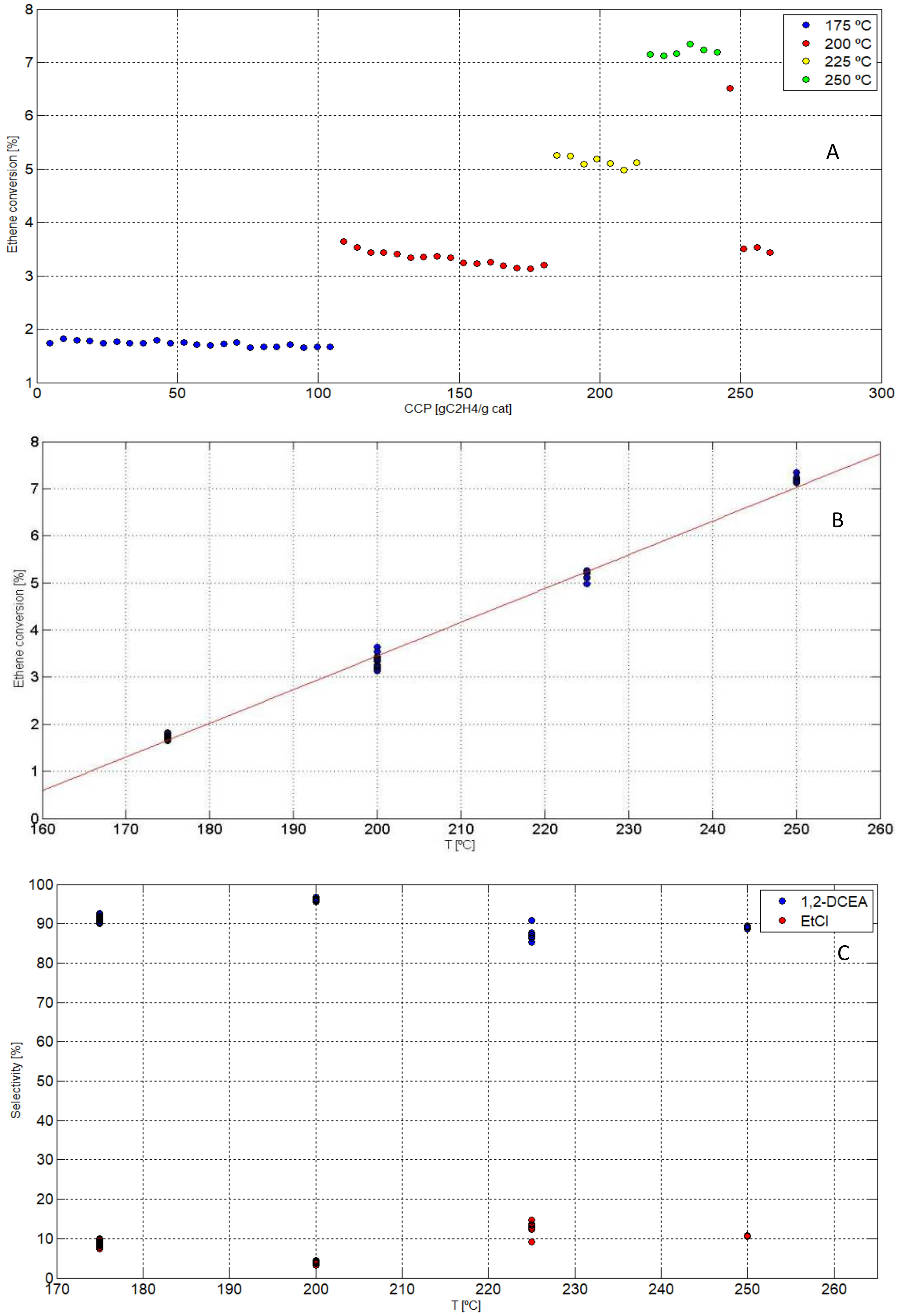


Fig. 5 Conversion at a time of ethylene (A) Influence of the temperature in the conversion (B) and selectivity of the different reaction products (C)

Like these results show, they are as they are expected, the higher the temperature is the higher the conversion. Furthermore, in the B plot can be observed a linear dependence with the temperature, indicating as expected that the rate increases linearly with the temperature. Besides, in these results the stability test is again showed, in the last three points at 200 ºC, the conversion is equal to the results at the previous time at 200 ºC. In the case of selectivity, the temperature has a strong effect on the selectivity of the different compounds of the reaction components. It showed that the increase temperature from 175 ºC to 200 ºC increase the selectivity towards 1,2 dichloroethane, but then increasing the temperature higher than 200 ºC decrease the selectivity towards 1,2 dichloroethane and favors the formation of ethyl chloride. In all the cases the selectivity of the interested compound, 1,2 dichloroethane, is higher than 80 %, showing a good behavior and results of the catalyst. These decrease in the selectivity can be explained maybe by coke formation during the reaction around the catalyst, making it difficult to the ethylene to reach the active site and react in the proper way.

3.2.3 CONCENTRATION OF THE DIFERENT COMPONENTS

In the case of the different components of the inlet reaction, oxygen and hydrogen chloride were changed to obtain its influence in the reaction, and its influence in the reaction rate for the case of the model developing.

EFFECT OF THE HYDROGEN CHLORIDE CONCENTRATION

In the case of hydrogen chloride, the initial concentration of this component was 9.5 % vol, the concentrations were decreased in equidistant intervals of 1.8 % until the concentration of 2.4 was reached. The temperature at which these experiments were carried out was 225 ºC. According to the works of Montebelli et al.[23] and Carruba et al.[24], the hydrogen chloride does not present any influence in the conversion, keeping it stable independent the concentration of it. But in the case of the selectivity, the lower the hydrogen chloride concentration is, the higher the selectivity towards 1,2 dichloroethane should be. The results are presented then:

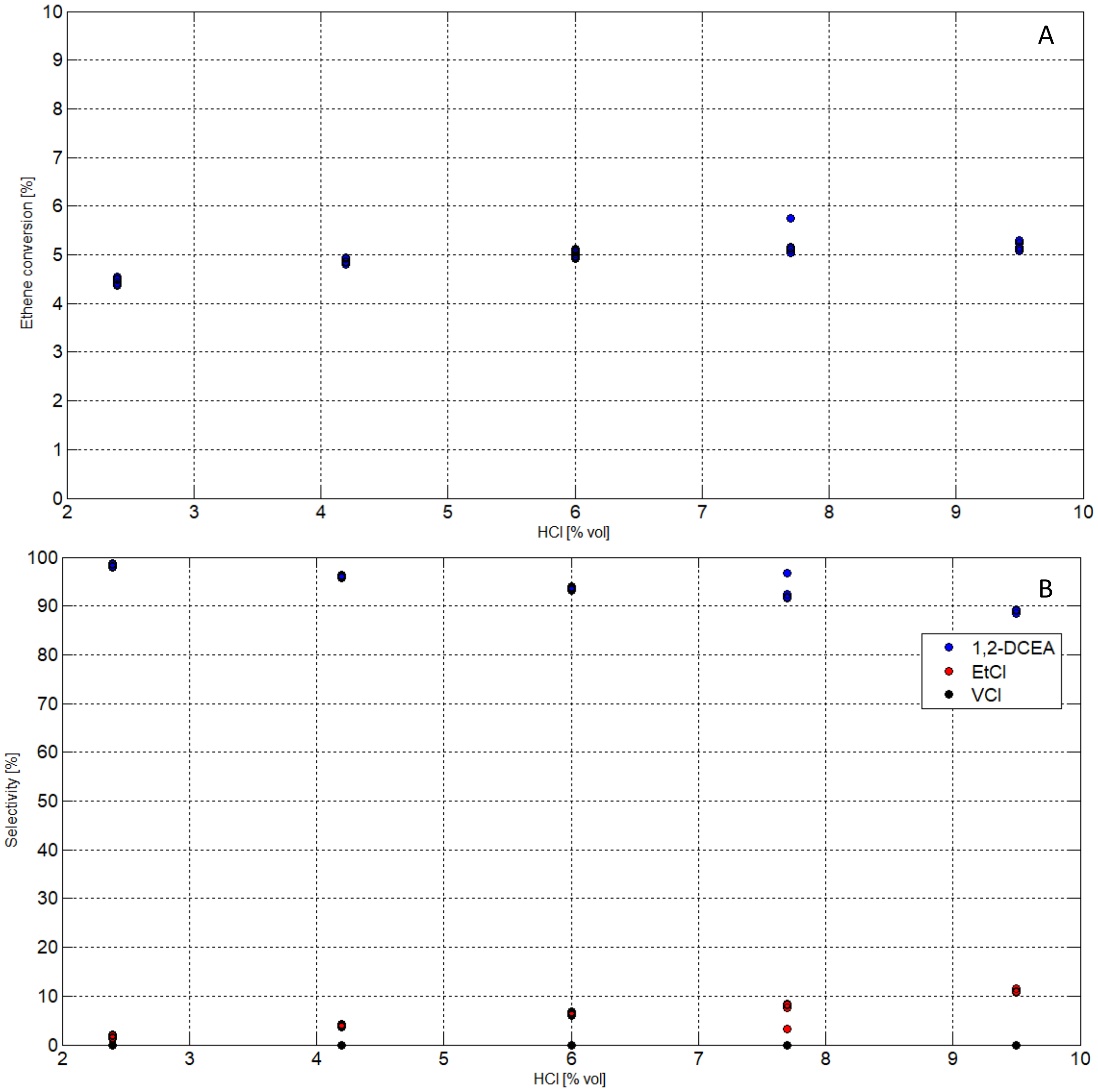


Fig. 6 Influence of the hydrogen chloride concentration in the conversion (A) Influence of the hydrogen chloride concentration in the selectivity of the different reaction products (B)

As the results show, and according to the bibliography, the conversion seems not to be affected by the concentration of hydrogen chloride, only in the case of a huge decrease in this concentration starts showing an effect in the conversion. It can be due to a run out of the specie, so it can lead to an impossible way to obtain more product of interest, 1,2 dichloroethane. In the case of the selectivity, it can be seen a clear dependence in the hydrogen chloride concentration. The steps of every concentration can be clearly differentiated, and it is the same behavior that the bibliography reports. The lower the concentration the hydrogen chloride is, the higher the selectivity towards 1,2-dichloroethane is. It can be concluded then that these results are good enough to be used in the develop of the model of the reaction.

EFFECT OF THE OXYGEN CONCENTRATION

In the case of oxygen concentration, the initial concentration of oxygen was 2.4 % vol of oxygen, and it was equidistantly increase in intervals of 0.8 % vol until the concentration of 4.3 % vol was reached and decrease in the same value until the concentration of oxygen was 1.1 % vol. The temperature at which these experiments were carried out was the same as in the case of the experiments with hydrogen chloride, 225 °C.

According to the works of Montebelli et al.[23] and Carruba et al.[24] the concentration of oxygen should affect to conversion decreasing it as the concentration of oxygen decreases as well as the selectivity. This can be explained due to the regeneration cycle that takes part in this reaction in the copper chloride catalyst, where the oxygen has a crucial part. According to the work of Leofanti et al.[21] this cycle is conformed of three reactions, which are:

$$2\,CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 2\,CuCl$$

$$2\,CuCl + {}^{1}/_{2}\,O_2 \rightarrow Cu_2OCl_2$$

$$Cu_2OCl_2 + 2\,HCl \rightarrow 2\,CuCl_2 + H_2O$$

So, this cycle can explain why decreasing the concentration of oxygen it decreases it conversion and its selectivity. The copper chloride is the one which give the chlorine to the ethylene, so the lower oxygen there is in the media, the lower coper chloride that can be formed again, so the less final product can be formed and more side product, because the first chlorination is easier than the second one.

The results are presented then:

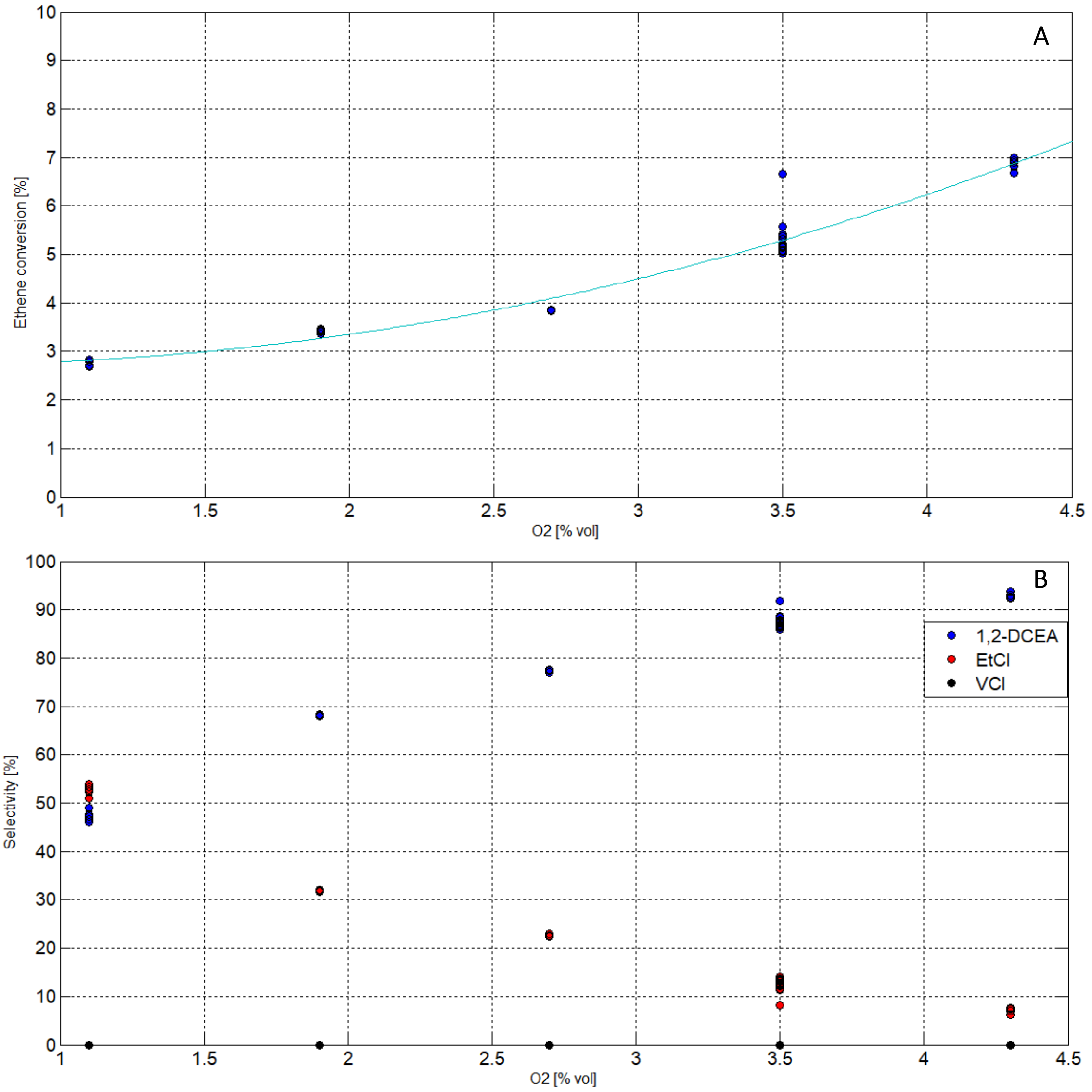


Fig. 7 Influence of the oxygen concentration in the conversion (A) Influence of the oxygen concentration in the selectivity of the different reaction products (B)

As the results show, they are like the bibliography describes, showing a decrease in the conversion as the oxygen concentration decreases. The decrease in the conversion seems to follow a second order equation approximately. In the case of the 1,2 dichloroethane selectivity, this decreases as well when the oxygen concentration drops, promoting the increase of the selectivity towards ethyl chloride. It can be also observed a slight deactivation of the catalyst, cause maybe due to the formation of carbon in the surface of the catalyst, explaining this decrease in the conversion when it was returned to the initial value of oxygen concentration.

3.3 COPPER CHLORIDE SUPPORTED OVER CERIUM OXIDE CATALYST

In this experiment, $CuCl_2/CeO_2$ was our catalyst previously prepared in the laboratory, using the procedure reported by Leino et al.[18] where they obtained a cerium oxide with a surface area of

126 m^2/g. The particle size used for these experiments was between 100 and 250 µm and the amount of catalyst used was 0.25 g of catalyst diluted in 8.5 g of glass beads. The temperature used for these experiments is 225 °C. This experiment is used to see the influence of a basic support, like cerium oxide, compared to an acid support like alumina. The results expected are a mixture of 1,2 dichloroethane, like the cupper chloride leads to 1,2 dichloroethane as main product in oxychlorination reaction, and vinyl chloride, because the cerium oxide leads to vinyl chloride as main reaction product according to the results of the work of Scharfe et al.[3].

The results are presented then:

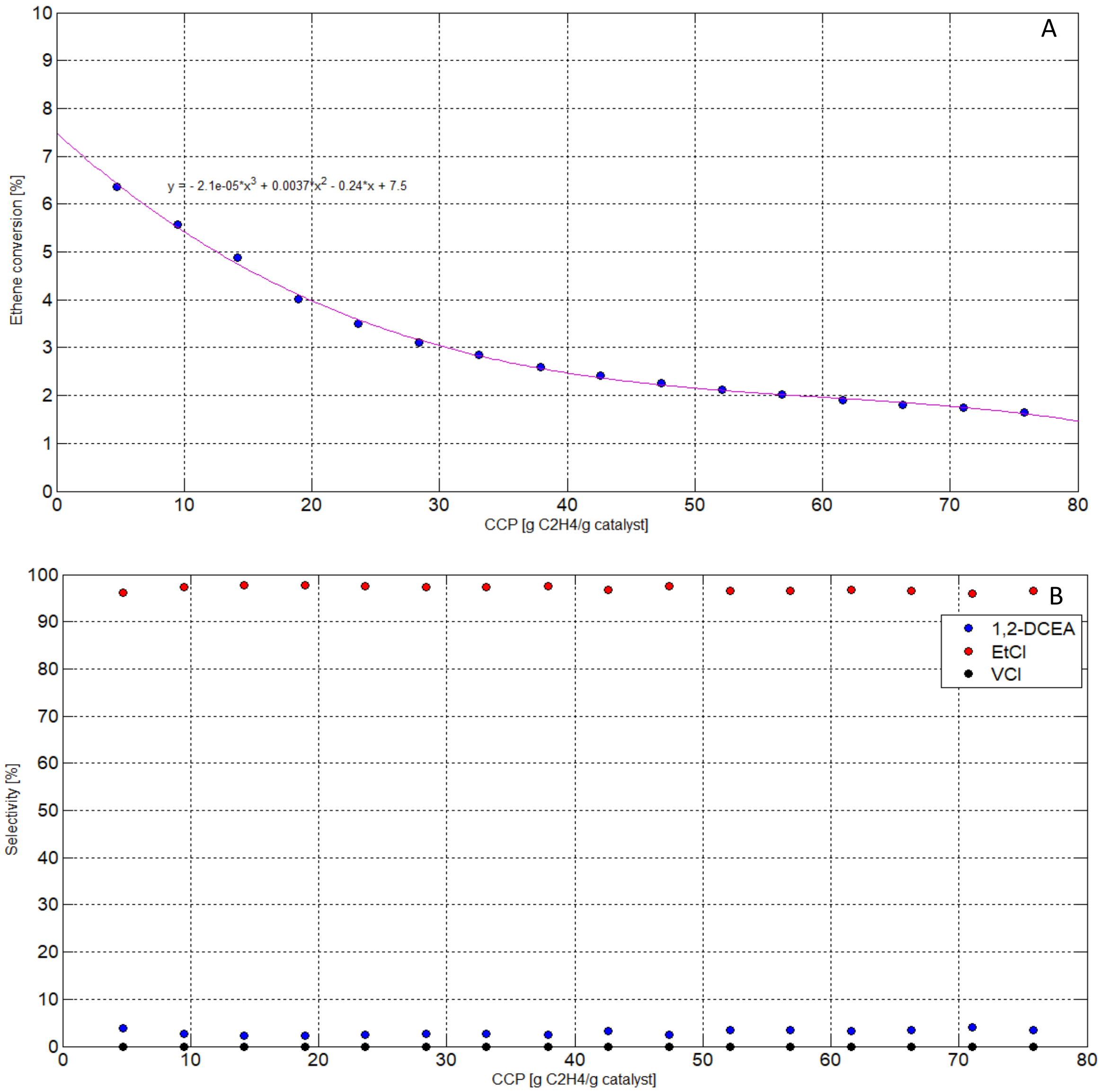


Fig. 8 Conversion of ethylene (A) Selectivity of the different reaction products (B)

These results show a fast deactivation of the catalyst. The conversion decreases fast, following approximately a third order equation, in time and seems to tend to 0% of conversion. Furthermore, the selectivity of the reaction products basically show that the main reaction product is ethyl chloride. This could be due to the sites characteristics of the support. CeO2 support is a basic support, and this quality is maybe affecting the copper as catalyst, avoiding to interact in the reaction and the only reaction taking place in this case is the direct hydrochlorination of the ethylene into ethyl chloride. This means that this is not a good catalyst. It deactivates rapidly, and the reaction products are not the interested ones. This catalyst was rejected for further experiments.

This also means that the support where the copper chloride is deposited has a crucial effect. This leads to a study of only the supports and the reactor empty itself. These experiments were carried out to confirm whether the catalyst is working or just this product are the expected ones for an empty reactor.

The results obtained are presented here:

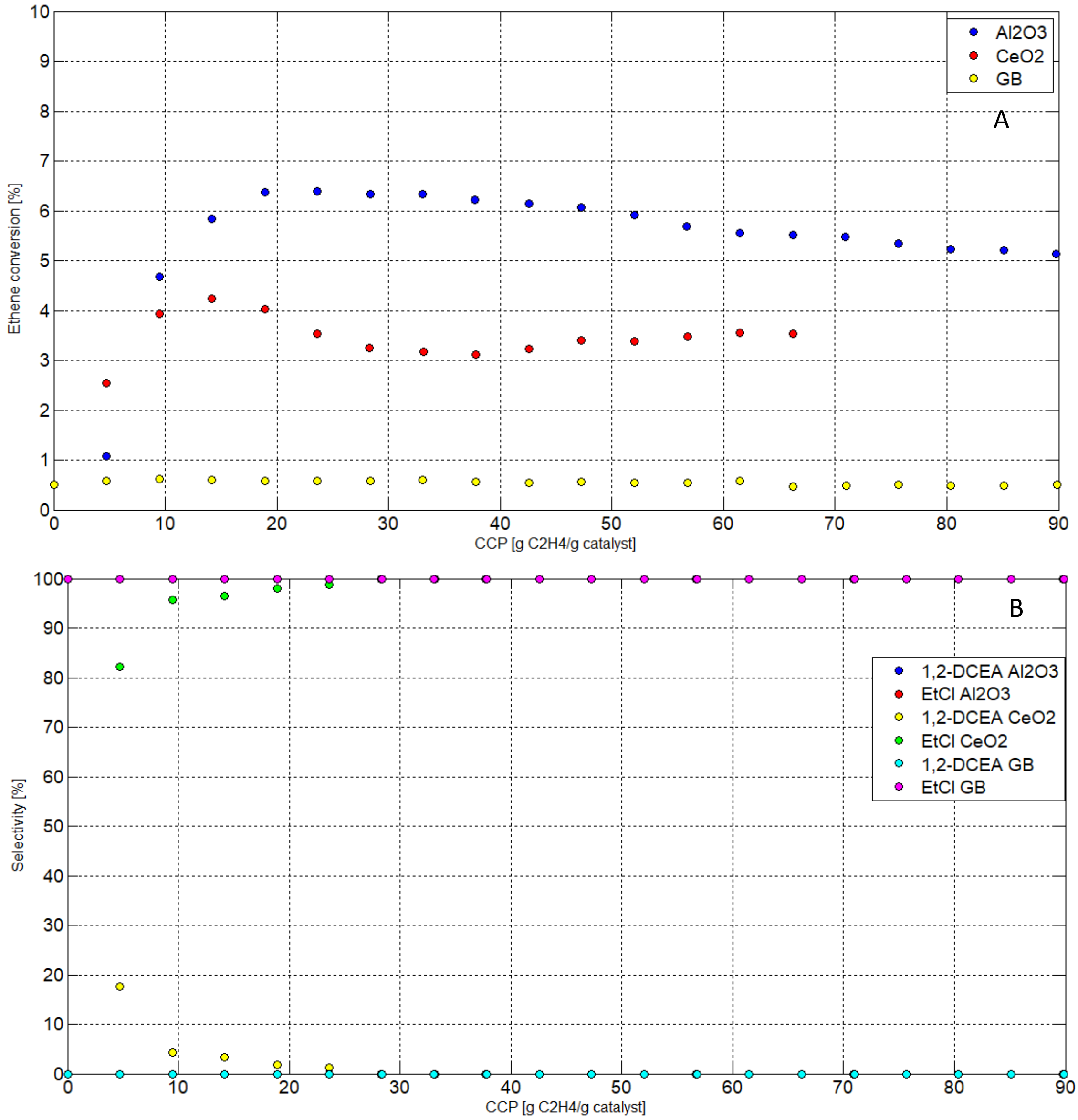


Fig. 9 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B) for every catalyst.

As the results show, the alumina present a conversion around 6 %, and only ethyl chloride is observed in the reaction products. In the case of cerium oxide, less conversion, around 3 %, is achieved. In this case in the first two analysis 1,2 dichloroethane was observed, after that the only product observed was only ethyl chloride. And in the case of the reactor with only glass beads, negligible conversion is achieved, less than 1 %. But in the case of selectivity, only ethyl chloride was observed.

It is seen that the support with acid sites, the alumina, present a higher conversion that the one containing the basic sites, the cerium oxide. This means that the chlorination of the ethylene seems to be promoted by a catalyst with acid sites. In the case of glass beads, they have silica, which also contains acid sites, which can explain the low conversion of the ethylene. In the case of the appearance of dichloroethane in the case of cerium oxide, it was reported by the work of Scharfe et al.[3] that at low temperatures, dichloroethane is seen. This can explain this appearance.

This support study can mean that the copper chloride needs acid sites to act as an active catalyst, meaning that in a basic support it cannot act at the same temperature or it is deactivated at all, not letting it to let the chlorine to the ethylene and the only product obtain is ethyl chloride by the hydrochlorination of the ethylene.

3.4 CERIUM OXIDE CATALYST

In the case of the cerium oxide catalyst, the first experiment carried was a stability test. This test was carried out to find out if the catalyst after several time is still stable. The catalyst was tested exposing it to a reaction time of several days.

The next step will be study the temperature dependence of the reaction with this specific catalyst. With this dependence, the energy activation can be calculated and compared with the activation energy in the case of the cupper chloride catalyst.

The last experiments carried out were the experiments changing the concentration of the reagents, specifically oxygen and hydrogen chloride. With these experiments, the relation between the reagents and the conversion and selectivity of the products can be found. With these results, the dependence in the kinetic equation of the components is found as well.

3.4.1 STABILITY TESTS

In the case of the stability test, the catalyst was operating during a period higher than 5 days. The inlet composition for this experiment was the same as in the case of cooper base catalyst. The temperature selected was 450 ^{o}C. According to the work of Scharfe et al.[3] the temperature should be around 400 and 500 ^{o}C to activate the catalyst and produce the reaction. The results are presented here:

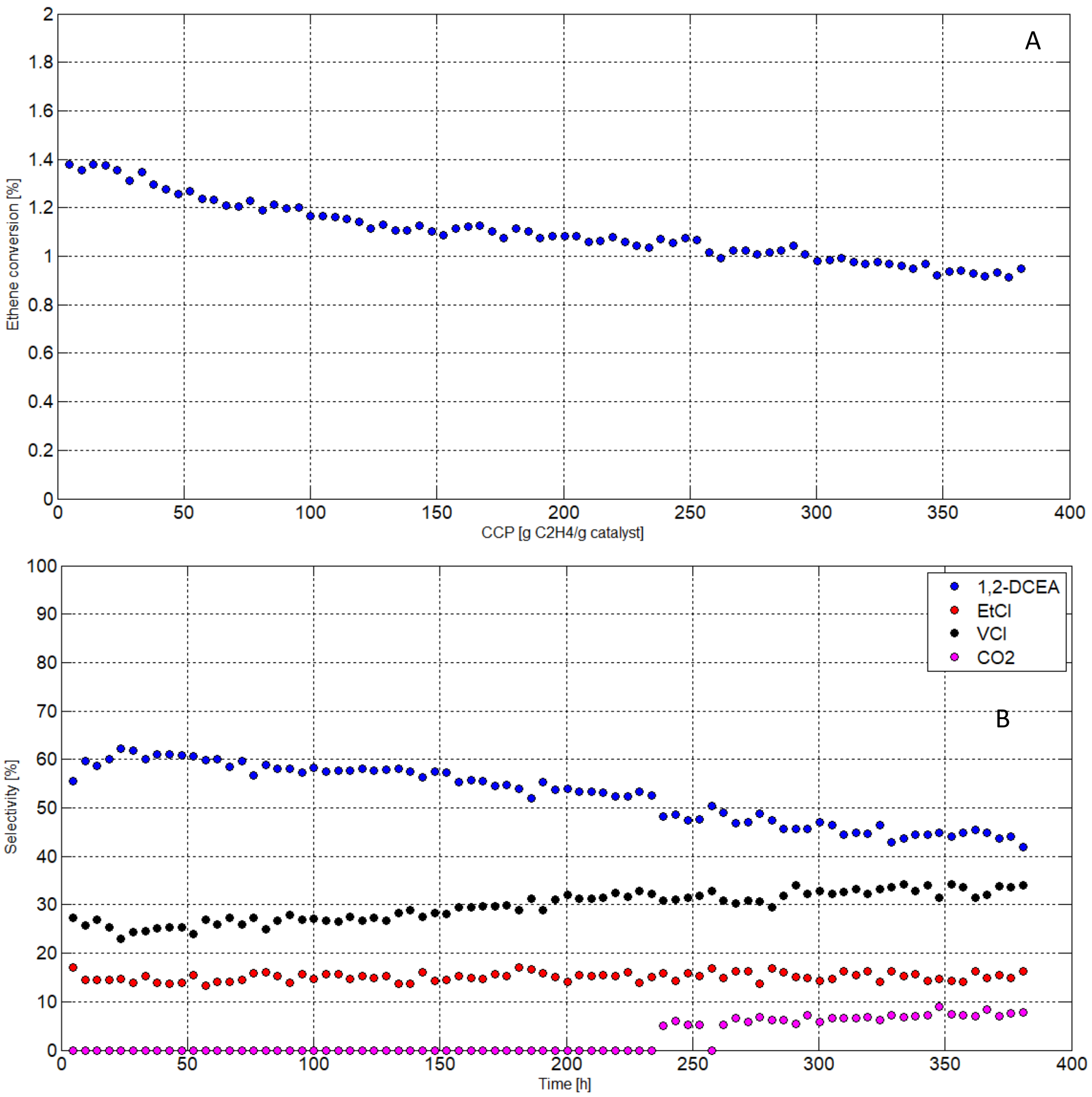


Fig. 10 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B)

In the results, it can be observed that the catalyst presents a small deactivation, is a deactivation of 0.2% in the conversion. It can be said that the deactivation of the catalyst is not negligible, due to it represents a 36 %. In the case of the reaction products, it can be seen an increase in the selectivity of the vinyl chloride and a decrease in the case of the 1,2-dichloroethane. Meanwhile the ethyl chloride remains quite constant. In the decrease of the 1,2-dichloroethane, it can be observed the appearance of carbon dioxide. This can be due to a deactivation of the catalyst and it provokes the direct oxidation of the ethylene to CO_2.

3.4.2 TEMPERTATURE DEPENDENCE

In the case of cerium catalyst, three experiments were carried out as well. The temperatures for this catalyst were 425, 450 and 475 ^{o}C. These experiments are carried out to develop a model and calculate the energy activation in the case of cerium catalyst and its dependence in the case with the temperature. The inlet composition of the reaction mixture was 30.4% vol. of ethylene, 2.7 % vol. of oxygen and 9.5 % vol. of oxygen, the rest 57.4 % vol. is nitrogen, an inert gas. The results expected are if the temperature increases, the conversion should increase as well. The main product expected are vinyl chloride, 1,2-dichloroethane and some ethyl chloride and maybe CO_2. The results are presented forward:

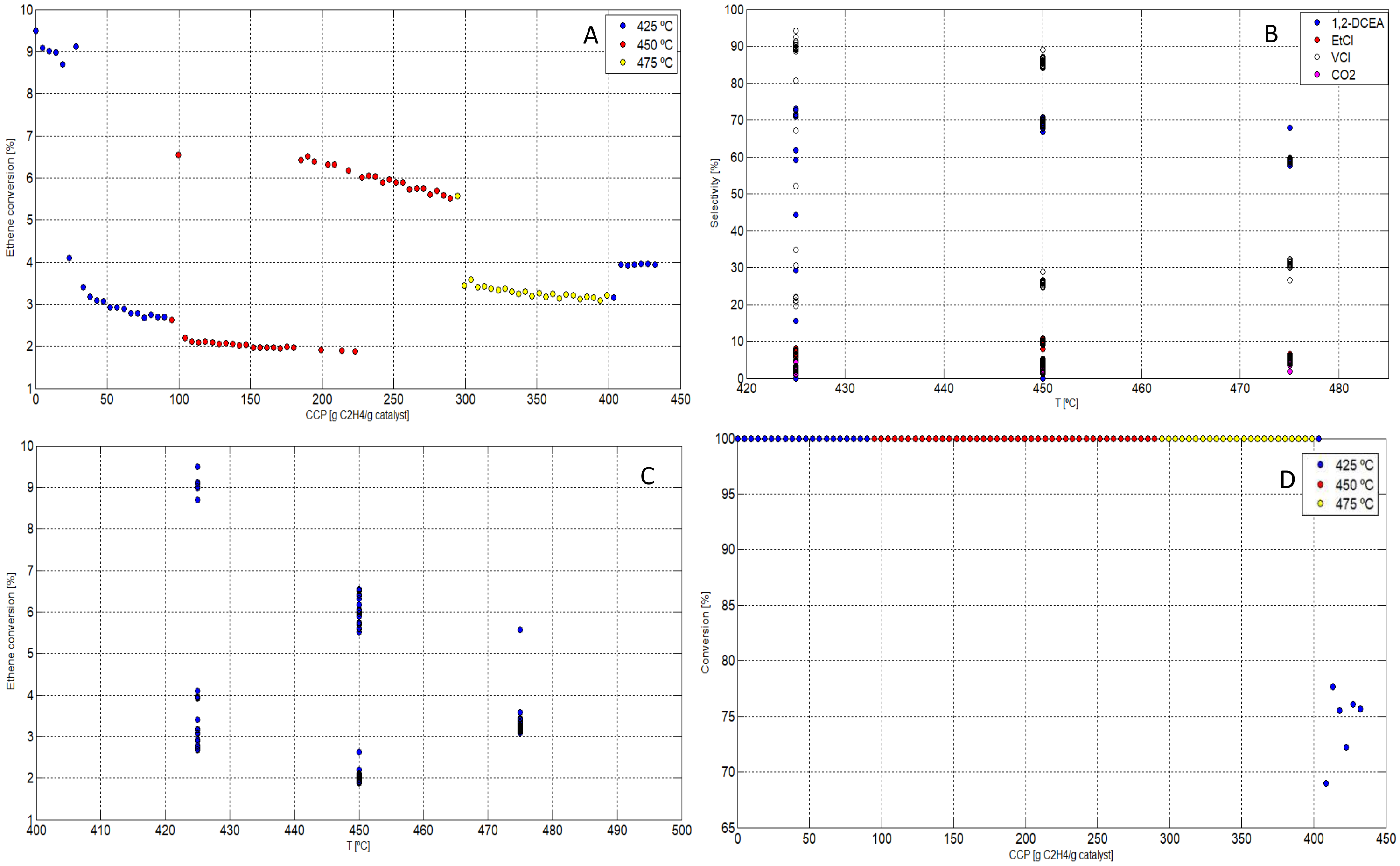


Fig. 11 Conversion of ethylene (A), selectivity of the different reaction products (B), Temperature dependence in conversion (C) and Oxygen conversion (D).

As the results show, there is a huge dependence in the case of temperature, but strange results for conversion were obtained in the case of 450 °C, where 2 stationary states were observed. This can be related with the O_2 consumption. As it can be seen, the O_2 consumption is 100 % for all temperatures. This can interfere with the results and may indicate that the catalyst is not working well or that the ratio ethylene:oxygen is too low. Another study was carried out with higher oxygen rate to verify the influence in the oxygen:ethylene ratio. Another strange behavior was observed in the case of 475 °C. In this case, the conversion is lower than in the other temperatures. This is abnormal but can indicate a change in the cerium oxide phase.

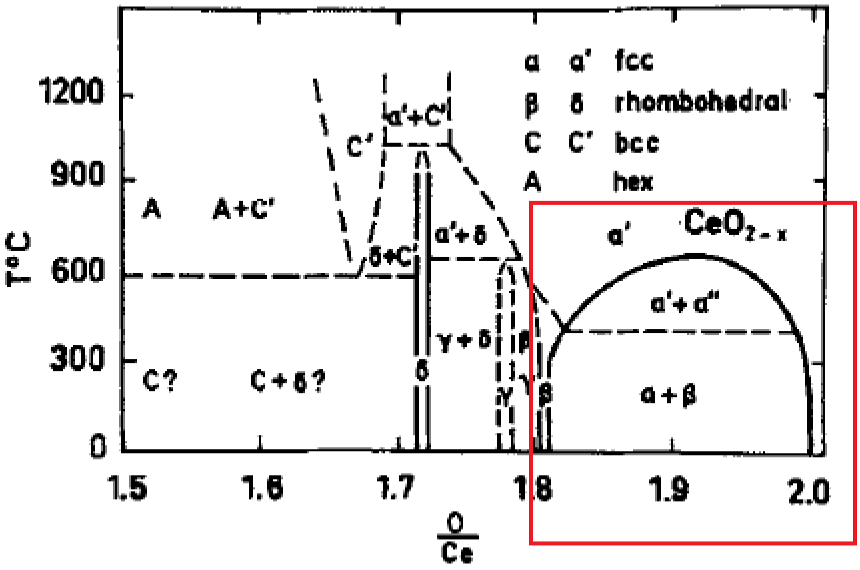


Fig. 12 Phase diagram for the system O/Ce[27].

As it can be seen in the phase diagram for O/Ce, in the red square, which is the area where the catalyst should be, for the case of 425 and 450 °C, the catalyst is in the same phase, the mixture of phases α and β. But in the case of 475 ºC, the phase changes, changing with it probably the absorption of the components in the catalyst, changing the conversion as well. This could be the explanation for this problem.

In the case of the experiment with higher oxygen ratio, the ratio of hydrogen chloride and ethylene was the same. The oxygen and nitrogen new ratio were 4.3% vol. in and 55.8% vol. respectively. The results are presented here:

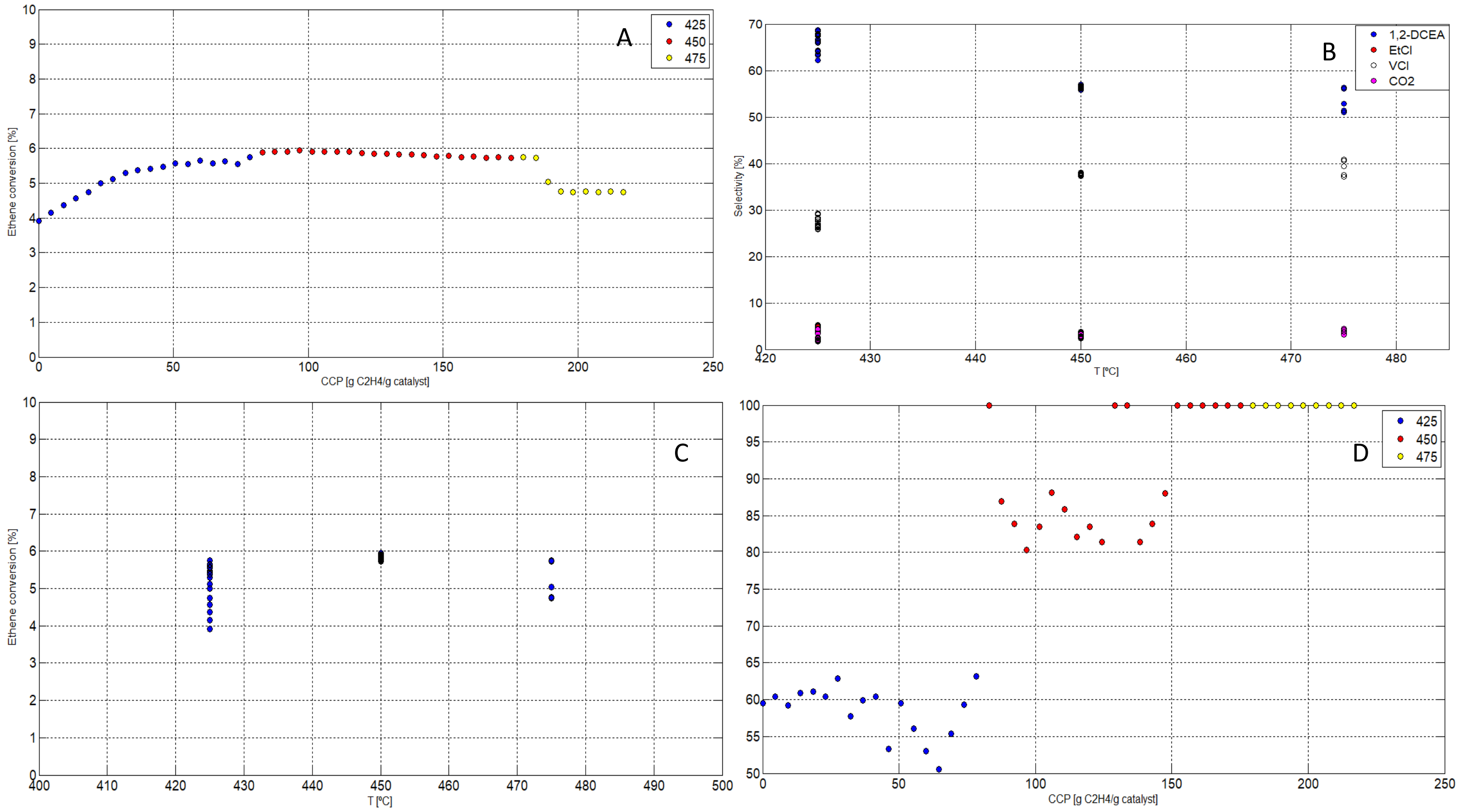


Fig. 13 Conversion at a time of ethylene (A), selectivity of the different reaction products (B), Temperature influence in the conversion (C) and oxygen conversion (D)

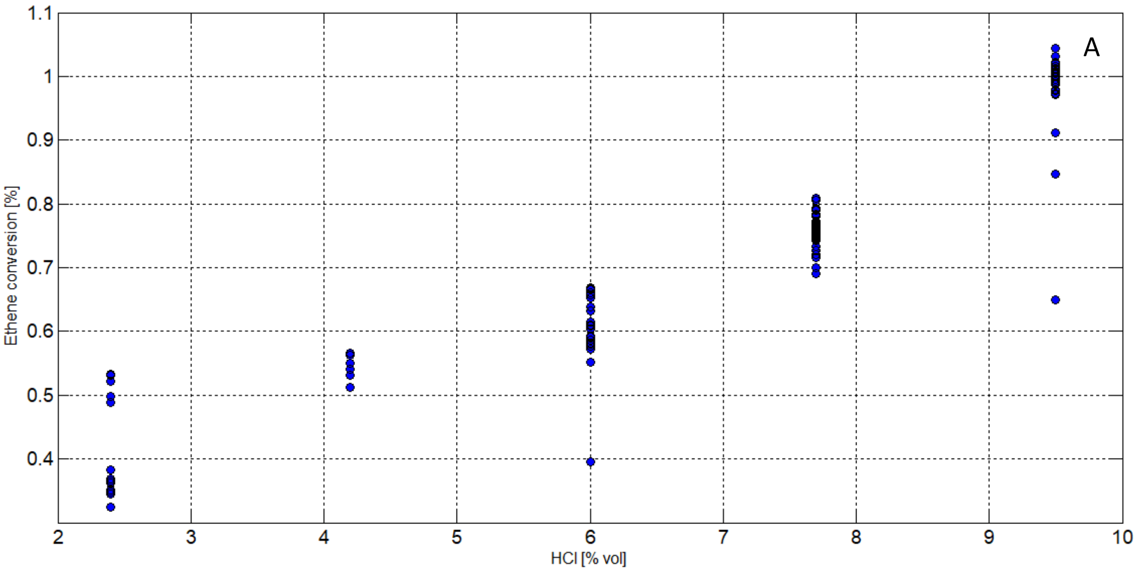
As it can be observed, in this case no different stationary points were observed in the case of 450 ºC. Furthermore, the behavior of the catalyst for the case of 475 ºC keeps constant. This confirm that the behavior at 450 ºC was caused by the consumption of the oxygen. The same behavior for the case of the different oxygen ratios can confirm the changes as well in cerium oxide due to the temperature and have nothing to do with the reaction components compositions at 475 ºC. In the case of selectivity, it can be observed in this case that the higher the temperature is, the higher the selectivity towards vinyl chloride is. This can be due to the higher temperature favors the dehydrochlorination of 1,2-dichloroethane into vinyl chloride.

3.4.3 CONCENTRATION OF DIFFERENT COMPONENTS

As in the work done in the case of cupper chloride catalyst, oxygen and hydrogen chloride were tested to identify its influence in the case of cerium oxide catalyst.

EFFECT OF HYDROGEN CHLORIDE CONCENTRATION

The initial concentration of the hydrogen chloride in these experiments was 1.1 % vol. The volume percentage was increased until it reached the concentration of 9.5 % vol in equidistant intervals of 1.8 % in volume. According to the work of Scharfe et al.[28], in the case of hydrogen chloride, the conversion should increase as the concentration of this component increases. The selectivity of the chlorinated components should increase as the selectivity of CO_x components decreases. The temperature at which these experiments were carried out was 450 ^oC. The results are presented here:



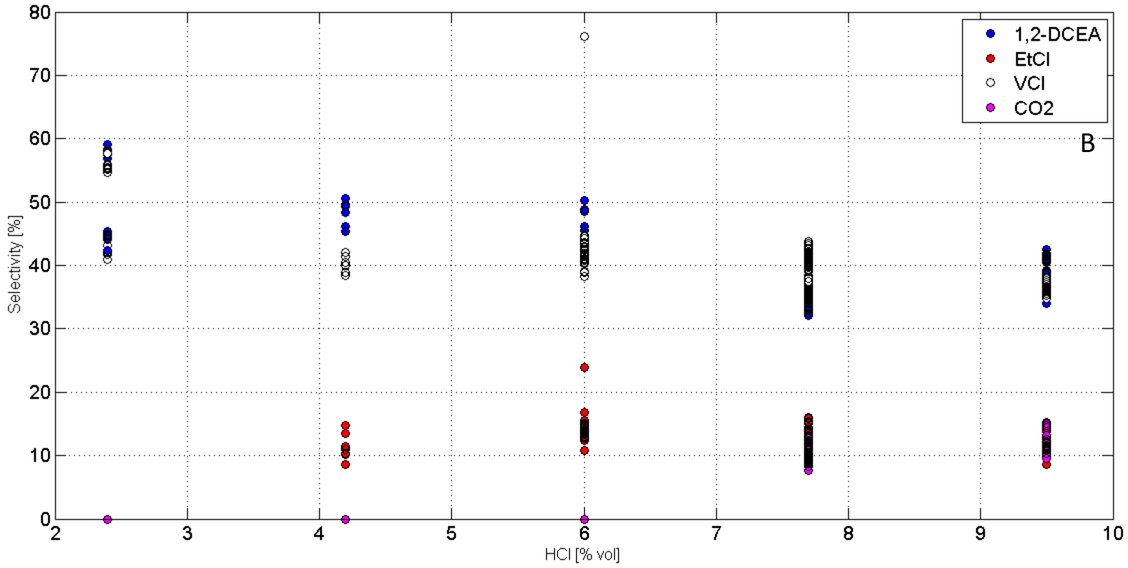


Fig. 14 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B)

As the results show, the conversion is increased as the concentration of hydrogen chloride increases. It seems to increase in linear dependence of the concentration of hydrogen chloride. This is the same as what was reported in the bibliography. In the case of selectivity of components, the selectivity of ethyl chloride increases as the concentration of the hydrogen chloride increases. This can be explained as an increase in the hydro chlorinating agents, the direct hydrochlorination of the ethylene is favored instead of the chlorination through the catalyst, obtaining then 1,2-dichloroethane or vinyl chloride. The increase in the ethyl chloride concentration of the last part at 1.1 % vol in hydrogen chloride can be explained by the deactivation of the catalyst. The less active the catalyst is the less vinyl chloride and 1,2-dichloroethane is formed. The explanation for the CO_2 must be the same. The less hydro chlorinating agents in the media and the deactivation of the catalyst leads the selectivity towards the products of the ethylene oxidation.

EFFECT OF OXYGEN CONCENTRATION

In the case of oxygen, the concentration of this components was initially 2.4 % vol. and was increased in equidistant intervals of 0.8 % until the concentration of 4.5 % vol. was reached. According with the work of Scharfe et al.[28] the oxygen should increase the conversion of ethylene, as the selectivity towards CO_2 is increase as the oxidative agents is increased. The temperature at which these experiments were carried out was 450 °C. The results are presented here:

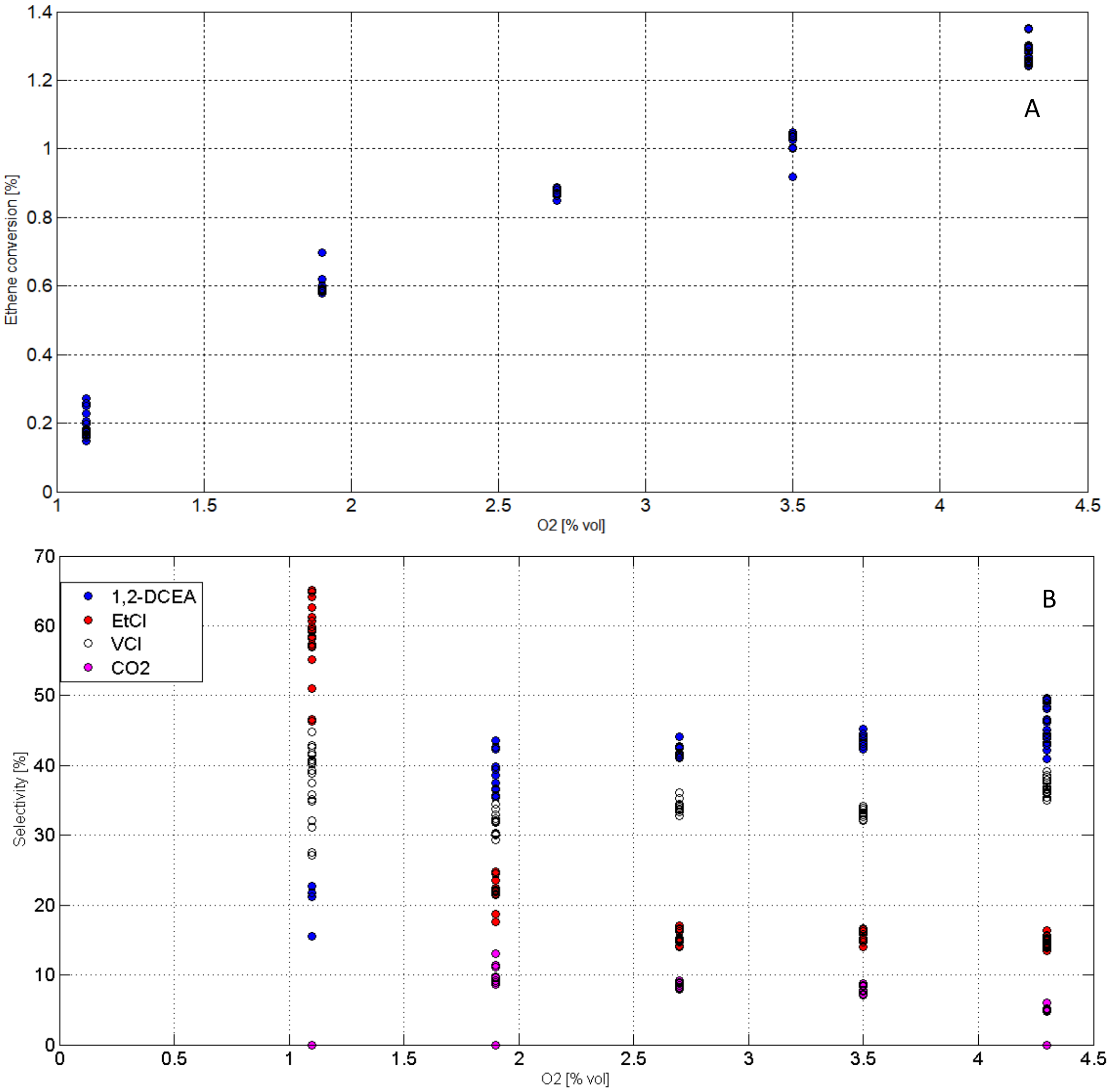


Fig. 15 Conversion at a time of ethylene (A) and selectivity of the different reaction products (B)

As it can be observed, the results fit the results reported in the bibliography, the conversion of oxygen is increased as the concentration of oxygen is increased. The CO_2 selectivity was also increased as the oxygen concentration increases in the inlet stream. What can be observed is also the hard dependence of the conversion of the reaction with the compound oxygen. When the concentration of oxygen was 2.4 % vol. it was so low that the conversion was only 0.2 % for the ethylene. This is something that must be considered, due to deactivation was not observed in the case of going back to 2.4 % vol. of oxygen.

3.5 OXYGEN CONVERSION

One interesting feature in this reaction is the use of two different catalysts and the use of two different temperatures for each catalyst. One behavior which is surprising is the change in the oxygen conversion comparing one experiment in the case of cupper chloride and other experiment in the case of cerium oxide. There is a huge difference in the oxygen conversion, which can lead, according to bibliography to a change in the reaction mechanism. According to the work of several authors, like Jones et al[25], who worked with chromium oxides for the oxidation of hydrogen chloride at temperatures between 325 and 355 ºC. Other authors studied the Deacon process[26], which uses a cupper chloride catalyst, like one of the catalyst used in this work, for the oxidation of hydrogen chloride working with temperatures between 350 and 400 ºC. All the authors report temperatures at least between 325 and 350 ºC minimum to start the reaction between these two components.

In the experiments using cupper chloride, the temperature is below those limits, which means that this reaction is not taking place, this means that the oxygen of the inlet mixture is only participating in the oxychlorination and in the oxidation of ethylene. But in the case of the cerium catalyst, the temperature is much higher, between 425 and 475 ºC, this is above the limit for starting the oxidation of hydrogen chloride reaction. This means that the oxygen in these cases, is reacting not only in the oxychlorination and ethylene oxidation reaction, is also oxidizing the hydrogen chloride and creating chlorine radicals, generating a new reaction mechanism for the oxychlorination and a direct way to produce vinyl chloride.

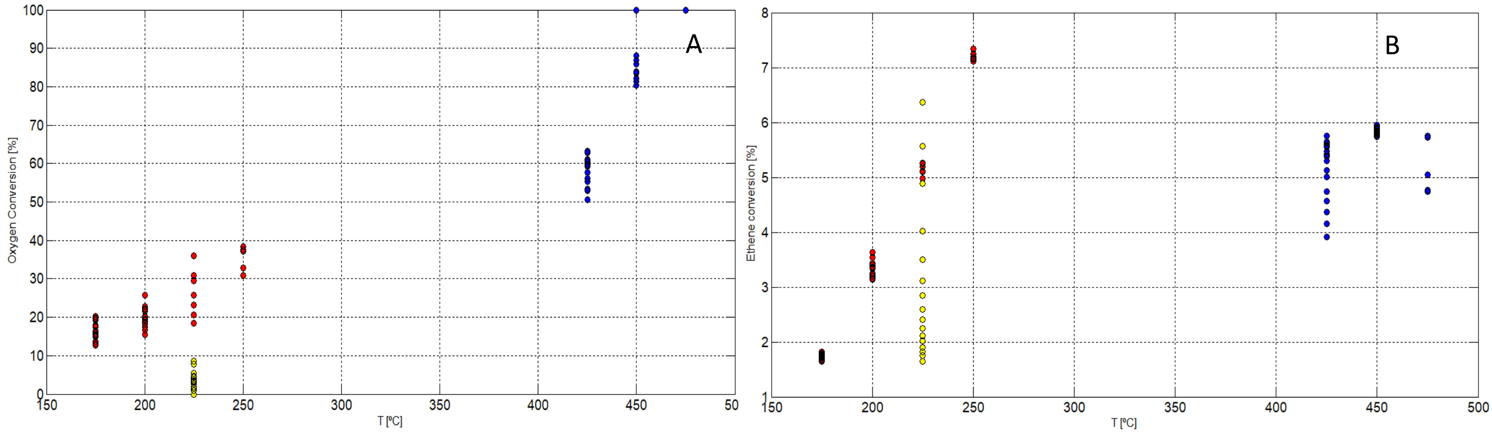


Fig. 16 Oxigen conversion(A) and ethylene conversion (B) for catalysts $CuCl_2/Al_2O_3$ (red), $CuCl_2/CeO_2$ (yellow) and CeO_2 (blue)

As it can be seen, the difference is huge. In the case of cerium oxide, the oxygen conversion is between 60 and 100 %, meanwhile in the case of $CuCl_2/\gamma Al_2O_3$ only reached a 40 % in some cases and in the case of $CuCl_2/CeO_2$ it barely reaches the 10 % of conversion.

3.6 MODELLING

3.6.1 COPPER CHLORIDE MODEL

According to the work of Montebelli et al. the oxychlorination over copper chloride kinetics has the following definition:

$$K_1 p_{C_2H_4} p_{O_2}^n \frac{p_{HCl}}{(1+K_1 p_{HCl})^2}$$

$$k_2 p_{C_2H_4} \frac{p_{HCl}}{1+K_1 p_{HCl}}\left(1-\frac{p_{C_2H_5Cl}}{p_{C_2H_4} p_{HCl} K_{eq,2}}\right)$$

Eq. 2 Rates for the formation of 1,2 dichloroethane and ethyl chloride respectively.

Using these equations for the modelling the results obtained for the yields of the different products are the following ones:

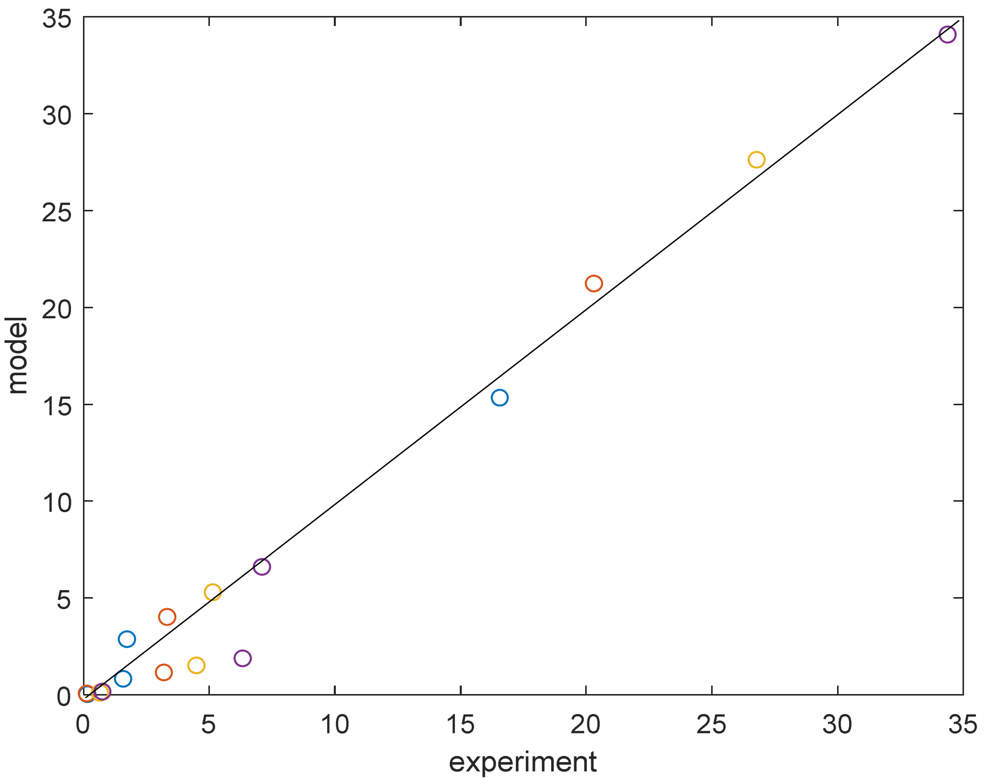


Fig. 17 Relation of yields between the model and the experimental data in the yields of the components.

As it can be seen, the model adjusts quite well the experimental data of yields of the different components. But the parameters obtained in the model are the following ones:

	Estimated parameters	Estimated std errors	Estimated relative standard error (%)	Parameter/std. error
K1	$8.51 \cdot 10^{-8}$	$8.35 \cdot 10^{-7}$	980.7	0.1
K2	$3.59 \cdot 10^{-9}$	$8.08 \cdot 10^{-8}$	2248.9	0.0
Ea1	$3.87 \cdot 10^{4}$	$7.44 \cdot 10^{4}$	192.3	0.5
Ea2	$4.45 \cdot 10^{4}$	$6.10 \cdot 10^{5}$	1370.0	0.1
KHCl	$4.44 \cdot 10^{-2}$	2.79	6272.9	0.0
Keq2	0.116	$1.81 \cdot 10^{2}$	156216.9	0.0

As it can be seen in the case of parameters, their deviation is very high. These data show that although the model fit the data, the parameters have a deviation too high to be reliable. Knowing this, the following work would be work more in this aspect and improve the model to develop a model with better parameters results and make it more reliable.

3.6.2 CERIUM OXIDE MODELLING

In the case of cerium oxide, the data definition for the reaction rates used was:

$$k_1 p_{C_2H_4} p_{O_2}^n \frac{p_{HCl}}{(1 + K_1 p_{HCl})^2}$$

$$k_2 p_{C_2H_4} \frac{p_{HCl}}{1+K_1 p_{HCl}} \left(1 - \frac{p_{C_2H_5Cl}}{p_{C_2H_4} p_{HCl} K_{eq,2}}\right)$$

$$\frac{k_3\, p_{C_2H_4} p_{O_2}^2}{1 + K_2 p_{HCl}}$$

$$k_4 p_{C_2H_4} p_{O_2}^n \frac{p_{HCl}}{(1 + K_3 p_{HCl})^2}$$

Eq. 3 Rates for the 1,2 dichloroethane, ethyl chloride, CO$_2$ and vinyl chloride respectively.

With these rates, the data obtained in the modelling were the following ones:

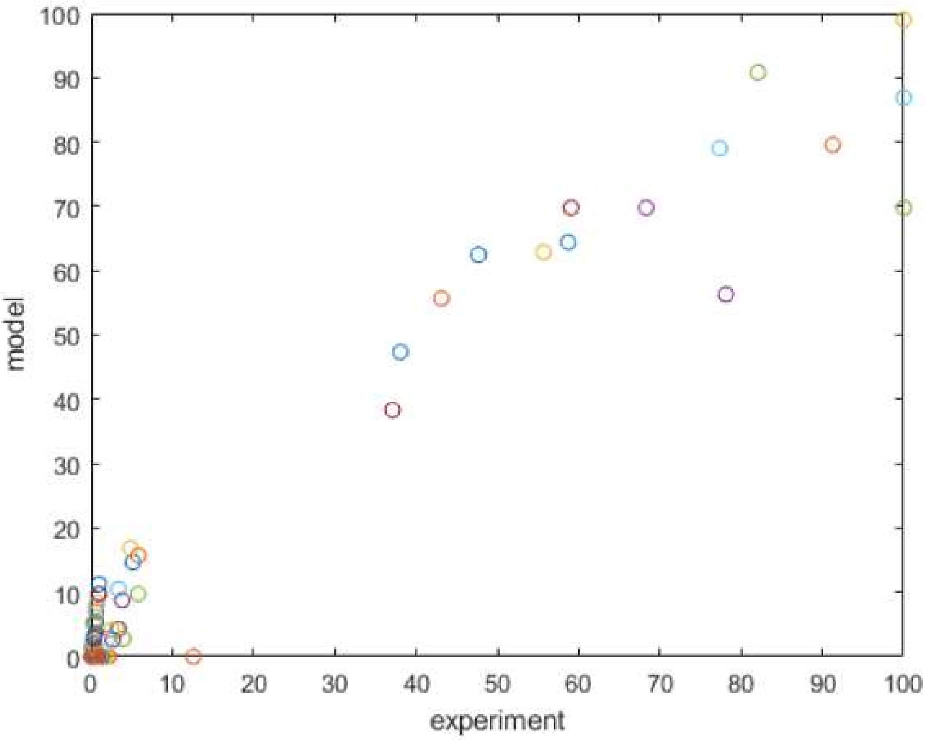


Fig. 18 Relation between the model and the experimental data in the yields in the case of cerium oxide.

The model has an explanation of the data of 93.4 %, but a deviation of the data of 5.323. This means that even the model seems reliable, it needs to improve the value of the parameters to fit the data with less deviation.

The values of the parameters in the equations are presented in the following table:

Estimated parameters

k1	$4.89 \cdot 10^{-7}$
k2	$4.63 \cdot 10^{-9}$
k3	$5.53 \cdot 10^{-8}$
k4	$4.07 \cdot 10^{-7}$
Ea1	$4.83 \cdot 10^{4}$
Ea2	$4.06 \cdot 10^{4}$
Ea3	$6.25 \cdot 10^{4}$
Ea4	$5.23 \cdot 10^{4}$
KHCl	$4.77 \cdot 10^{-2}$
Keq2	$5.73 \cdot 10^{1}$
K2	0.618
K3	0.835

These parameters are not reliable for a scale-up for the process, even though they seem to be to fit the experimental data, as in the case of copper chloride.

This can be caused due to the large number of parameters that have to adjusted in the model, concluding that these experiments are not enough to develop a reliable model and more investigation should be done in this topic.

4. CONCLUSIONS

In this work the oxychlorination of ethylene was studied using three different types of catalyst, copper chloride over γ-alumina, copper chloride over cerium oxide catalyst and cerium oxide catalyst. All catalyst showed different behaviors, showing that the $CuCl_2$/γ-Al_2O_3 catalyst works at lower temperatures such as 225 °C. An Arrhenius behavior in the case of the dependence with the temperature was observed as expected, increasing the conversion while the temperature increases. It also has strong dependence in the case of oxygen for the ethylene conversion and for 1,2-dichloroethane selectivity. But in the case of hydrogen chloride only dependence in the selectivity towards 1,2-dichloroethane was observed, increasing the selectivity while the concentration of hydrogen chloride decreases. The conversions obtained were around 5 % with this catalyst and selectivity towards 1,2-dichloroethane over 90 % were achieved, showing that this catalyst is a very promising one. The working point for this catalyst should be at the highest temperature and oxygen composition and the lowest hydrogen chloride composition in the inlet mixture, maximizing the conversion of ethylene and selectivity towards 1,2-dichloroethane.

In the case of cerium oxide, the temperatures of work needed were much higher, around 400 ^{o}C. The temperature dependence showed no Arrhenius behavior, showing that other effects must be considered, such as oxygen adsorption in the catalyst. Phase changes in the cerium oxide are also possible working over 450 ^{o}C. The oxygen and hydrogen chloride showed a huge dependence with the ethylene conversion, increasing it while the concentration of these two reagents is increased. In the case of selectivity, for hydrogen chloride only ethyl chloride selectivity increases as the concentration of this reagent increases, keeping the selectivity towards 1,2-dichlroethane and vinyl chloride almost constant. The CO_2 selectivity increases while the hydrogen chloride composition decreases, meaning that a lack of hydro-chlorinating components leads to an oxidation of the ethylene. For the case of oxygen, the selectivity keeps constant as well for the case of vinyl chloride. The increase in the selectivity of CO_2 is explained by an increase in the case of oxidizing agents in the media as the oxygen conversion increases. And for the case ethyl chloride and 1,2-dichloroethane, if the oxygen concentration drops hard, the direct hydro-chlorination of ethylene can take place easily, as well as the dehydrochlorination of the 1,2-dichloroethane formed. The less oxygen concentration in the media avoid the oxychlorination of ethylene, but a huge amount of oxygen leads to the oxidation of ethylene. In this case a compromise must be arranged between the conversion of ethylene and the selectivity of vinyl chloride and 1,2-dichloroethane. Conversion around 5 % were achieved with this catalyst and selectivity towards vinyl chloride and 1,2-dichloroethane were over 90 % of total selectivity in most of the cases. The working point for this catalyst should be a temperature of 450 ^{o}C to avoid the phase change of cerium oxide and a concentration of hydrogen chloride minimal to achieve the highest selectivity towards vinyl chloride and 1,2-dichloroethane, and a concentration of oxygen around 2.5 % to maximize the conversion minimizing the selectivity towards CO_2.

In the case of the modelling, the model for copper chloride fit the data but the large deviation in the data showed that it is not a reliable model. The same case is for cerium oxide, in which the model seems to fit quite well the data but the large deviations in the parameters showed that the model is no reliable enough to use for further applications. This could be caused due to the large number of parameters that the model has to fit, especially for the case of cerium oxide, producing these huge deviations in the values of the constants of the model. More investigation should be done in this topic to develop a reliable model considering copper chloride and cerium oxide catalysts and to develop an industrial process with these catalysts.

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