Oxidation of α-pinene

Preparing and testing different types of niobium silica catalysts to see if they will provide value-added products

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ABSTRACT

The aim of this project was to test the possibility of oxidizing α-pinene with different catalysts that had silica as support and niobium as the active component. To see if they had oxidizing abilities, the catalysts were tested by analyzing their products in a GC and GC-MS. Results showed that the products contained value-added products. The different catalysts had either Si-SBA-15 or dense SiO₂ as support. For adding niobium, four different addition methods niobium were used to create nine different catalysts: impregnation, grafting, incorporation and a modified version of incorporation. The challenge of doing standard incorporation was to make niobium hydrolyze at the same pH as silicon, even though silicone hydrolyses at about pH 1 while niobium needs a higher pH for that reaction. The outcomes from testing nine different silica catalysts with niobium were that the main resulting product was pinocarveol, a very expensive substance that is used in cosmetics [1]. Verbenol, verbenone, pinene oxide and campholenic aldehydes, which are the usual products resulting from α-pinene oxidation, were only found in low amounts. Another interesting result was that grafted Nb-SBA-15 had much higher conversion than the Nb/SiO₂ which shows that an increase of the surface area improves the catalytic ability.
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INTRODUCTION

The pulp industry in Sweden uses pine trees as raw material for its production. Heating of the wood chips makes the turpentine evaporate. The volatile turpentine is collected as a byproduct and then either sold or burned depending on the oil price. It is a mixture of products and can be separated through additional separation processes. One of the products that it contains is α-pinene. [2,3]

In this project α-pinene was chosen as the raw material because it is a cheap material that is produced in an industrial scale and because it is a reactive molecule. There are many expensive products that descend from α-pinene that are used in perfumes and in the pharmaceutical industry [4]. The purpose of this project is to produce a catalyst that turns α-pinene into a value-added product with high selectivity. Earlier research on niobium with silica as support has shown good oxidation results when oxidizing methanol with Nb-MCM-41 and Nb/SiO2 as catalysts [5]. But in this project, Nb-SBA-15 will be used instead of Nb-MCM-41 because of its large surface area, tuneable pore sizes, stable structure at high temperatures and acidic surroundings [5].

The standard products received from oxidizing α-pinene are: verbenol, verbenone, pinene oxide and campholenic aldehydes, but the main product obtained in this project was the rare product pinocarveol (Fig. 1). That makes this to an interesting project to continue working on. [6]

![Chemical structures](image)

**Figure 1:** The most likely products obtained from α-pinene oxidation: I Campholenic aldehydes; II Verbenol; III Verbenone; IV Pinanediol; V Pinocarveol; VI p-Cymen-8-ol will be referred to as Cymenol; VII α-pinene.
Catalysis

Several different catalysts are produced, tested and evaluated to get an idea of how to make them more effective and selective. Each catalyst is tested with α-pinene and the resulting oxidation-products are analyzed to see how well the catalyst works.

Catalysts are an important part of today’s society. Perhaps the most common one people think of when mentioning catalyst is the one in the car exhaust system. Other important uses for catalysts are in chemical and fuel production, where the majority of products have been in contact with at least one catalyst. A catalyst can help with pollution problems, makes reactions more efficient, and so-called selective catalysts reduce waste.

The principle of how a heterogeneous catalyst works is that a molecule gets adsorbed onto its surface, which changes the bonds in the molecule and thereby leads to reactions happening on the surface. After that the molecule desorbs from the surface as a new molecule.

Heterogeneous catalysts are improved by a porous structure and can be made of e.g. oxides like alumina, titania or silica. Some other types of supports for catalysts are metals, organo metallic complexes and enzymes. [7]

The same oxide can have different structures that are beneficial for different things, e.g. some structures have a larger surface area but weaker walls that collapse at high temperatures while others have a smaller surface area but the walls can tolerate high temperatures and acidic environments.

In this project the catalysts were be made with silica as the support. There were two different kinds of silica; SiO₂ and SBA-15. SiO₂ are dense particles and do not have an as large surface area. SBA-15 has a porous structure where the pore size can be tuned to a specified size.

The silica oxide provides a surface were a reaction can take place but it cannot catalyze any reactions without active sites. These active sites are often different metals that can produce different results on a substance depending on the conditions. The way active sites are created on the catalyst differs: impregnation, grafting and incorporation of the metal are the methods that were used here. [8]

Previous studies on niobium on silica oxidising methanol obtained very good results [9]. Gao and colleagues compared Nb-MCM-41 with Nb₂O₃/SiO₂ and concluded that the active sites on the respective catalysts had similar reactivity/selectivity, but the
Nb-MCM-41 had a higher activity due to the larger surface of the niobium which provides more active sites on the catalyst.

The good results made it interesting to explore the possibility of changing the oxidised product from methanol to α-pinene. The fact that niobium and silica worked so well together made the option of testing a third type of support based on silica intriguing. [9]

SBA-15 is prepared with a triblock copolymer and silica in the form of tetraethyl orthosilicate, later called TEOS, in a very acidic environment at about pH 1. This limits the amount of metals that can be incorporated into the structure. To make the metal ion incorporate into the silica structure it needs to hydrolyze at the same pace as the silica, but most metals do not hydrolyze at this low pH. Niobium is one of those metals that should not be able to be incorporated and it was part of this project to see if there was a way to incorporate it despite these difficulties.

![Figure 2: TEM image of the SBA-15 structure.][6]

As can be seen in fig 2, SBA-15 has a honeycomb structure which provides the large surface area. One of its advantages is the fact that it can tolerate acid which makes it easy to reactivate from heavy metal poisoning. The fact that the pore sizes can be tuned is a big advantage when it is used for separating particles by size as a stationary phase for high-speed CEC separation[10]. Another beneficial characteristic of SBA-15 is its wall thickness that makes it very stable at high temperatures, even at high temperatures with steam in comparison to MCM-41 that cannot tolerate temperatures as high as that. [5,8,11,12]
Product analysis

A GC-FID and a GC-MS will be used to test what kind of products the catalysts produce.

GC stands for gas chromatography and the basic principle is that a sample is injected into the machine and is heated up so that it evaporates into gas phase. The gas is then helped into a colder separation column by a carrier gas; this gas is constantly going through the column to help the sample forward. In this project, hydrogen was used as carrier gas.

The column is designed to separate the different molecules in the sample. The principle of the separation is that different molecules interact with the stationary phase. The interaction is different depending on the molecule; small volatile substances pass through the column first. Depending on the amount of interaction with the stationary phase, the molecules exit the column in a specific order. The temperature in the column increases slowly to help the slower products through.

When the products are separated they are taken to a detector where there are some different options to choose from. The two used in this project are FID and MS.

FID stands for flame ionizing detector and the principle is to burn the product that comes from the column together with hydrogen gas and air. Carbon atoms (except carbonyl and carboxyl carbons) then produce a CH radical that is meant to produce a CHO$^-$ and an electron - but only about 1 in $10^5$ CH radicals does that. These ions are detected and the resulting signal is proportional to the number of susceptible carbon atoms.

MS, mass spectroscopy, is another type of detector that can tell what the product is. Different from FID, MS only tells that there is a product containing carbon atoms. It provides both qualitative and quantitative data. MS has three parts; first the ionization that breaks the products into positive ions, then the products pass through an electromagnetic field that sorts the ions after their mass and charge, and last a detector that counts the number of ions of a specific weight and charge. [13,14]
EXPERIMENTAL

General information
Four different types of additions of niobium were used on two types of supports.

Impregnation of 2, 5 and 10 wt% Nb on SiO₂ using NbCl₅
Impregnation of 2, 5 and 10 wt% Nb on Si-SBA-15 using NbCl₅
Incorporation of niobium to Si-SBA-15 using niobium oxalate
Modified incorporation of niobium to Si-SBA-15 using niobium oxalate
Grafting niobium to Si-SBA-15 using niobium ethoxide

This gave a total of 9 different catalysts which were all tested by reacting with 98% pure α-pinene. As an oxidant, tert-Butyl hydro peroxide (TBHP) or hydrogen peroxide (H₂O₂) were tested and as a solvent CH₃CN was used. The products of the reactions were analyzed with a GC-FID and GC-MS.

Chemicals used
The surfactant for SBA-15 pluronic 123 (P123, three block copolymer) mol wt. 5800 g/mol, received from Sigma-Aldrich
For oil bath paraffin oil light from AppliChem
Acid for SBA-15 hydrochloride acid 37% MW 36.46 g/mol, 1.18 kg/l from VWR
Silica for SBA-15 Tetraethyl orthosilicate (TEOS) MW 208.33 g/mol from Aldrich
Ethanol 99.5% for dissolving NbCl₅, Solveco analytical grade
Millipore deionised water, will be referred to as Distilled water
Niobium(V)ethoxide 99.95% trace metal basis MW 318.21 g/mol from Aldrich
Niobium(V)oxalate hydrate Powder FW 538.04 g/mol from Alfa Aesar
Niobium(V)chloride 99% MW 270.17 g/mol from Aldrich
Acetone from Aldrich, used for washing
α-Pinene 98% MW 136.28 g/mol from Aldrich
Hydrogen peroxide 30 wt% AnalR NORMAPUR from VWR
tert-Butyl hydro peroxide (TBHP) 70 wt% in water FW 90.12 g/mol
Acetonitrile isocratic grade for liquid chromatography from Merck

~ 9 ~
Preparation of catalysts
The foundation of this project is the catalyst because there will be a reaction between peroxide and α-pinene in a good solvent even without the catalyst, but the reaction will be a lot slower. The aim by using a catalyst is to improve the conversion, achieve high selectivity, obtain as low amount of byproducts as possible and hopefully get unordinary products.

**Figure 3**: A Oven that was used during the preparations of the catalysts. B Inside of the furnace with dry SBA-15 which is a very fine white powder. C Outside of the furnace that was used during the preparations. D Schematic picture of the Dean Stark apparatus used while preparing grafted Nb-SBA-15.

Preparation of Si-SBA-15

```
Oil bath at 40°C

20 g P123 dissolved in 150 mL distilled water
  ↓  Stir
Add 600 mL of 2 M HCl
  ↓  Stir for 3h
Add 42.5 g of TEOS
  ↓  Stir for 24h
Age in oven at 95°C for 48h
  ↓
Filter and wash with water and then ethanol
  ↓
Dry over night in 90°C
  ↓
Calcinate at 600°C for 6h
```

**Scheme 1**: General procedure for preparing Si-SBA-15 [5]
An overview of the procedure that is presented below can be seen in scheme 1. First, 20 g of P123 (19.975 g) were put into a 2000 mL polyethylene bottle. It is important to make sure that all of the P123 goes to the bottom and does not get stuck on the walls because otherwise parts are not included in the reaction. P123 is a dense and sticky substance so it is hard to get the exact amount into the bottle. A measuring cylinder was used to add 150 mL of distilled water to the P123.

A large stirrer was added to the P123 to provide sufficient stirring. It is important to have appropriate amount of stirring. Too vigorous stirring can cause formation of bubbles because P123 has soap-like properties. If bubbles form some of the P123 is not included in the reaction and the catalyst yield is lower. A too slow stirring limits the mass transport, which also would result in a lower yield. The only way to know if the stirring is good enough is to look into the bottle and make an assessment.

The bottle was placed in a regulated oil bath on a hotplate stirrer. The temperature was set to 40°C and the bottle was forced into the oil bath with clamps attached to bars in the fume cupboard. Before stirring was initiated, the bottle was closed tightly.

While the mixture was stirred, 600 mL of 2 M HCl were prepared by first adding 497 mL of distilled water into a 1000 mL plastic bottle using a 250 mL measuring cylinder, and then adding 103 mL of 37% HCl using a measuring cylinder for the first 100 mL and then a graded pipette to add the last 3 mL. The calculations for this mixture were however wrong, since it was calculated on the assumption that 37% HCl is 11.65 M. In reality it is 12 M which makes the right amounts 100 mL of HCl and 500 mL of distilled water calculated from $V_1 N_1 = V_2 N_2$ were $N_1=12$ M HCl start concentration, $V_2=600$ mL as the total volume and $N_2=2$ M HCl the final concentration.

The HCl solution was stirred a little and then added to the mixture. Afterwards the cap was tightly secured on the bottle and the bottle was left for stirring for 3h at 40°C.

The solution stirred for 3.5h, which, in contrast to a too short stirring time, does not have any bad effects on the reaction.

During the stirring, 42.5 g of TEOS (42.63g) were weighed. The TEOS was added into the bottle using a plastic 2 ml pipette. Since the speed of addition is important, it was done drop by drop to make sure to get an even distribution of the silica in the solution. Addition has to be done quite fast so the time between the first and the last TEOS reaction is not too long. Then the cap was tightly secured and the reaction was left stirring for 24h in a 40°C oil bath.

After 24h, the bottle was removed from the oil bath and its cap was tightened once more. Except for a negligible small mark in the bottom, the bottle was free of cracks.
To lower the risk of HCl vapour corroding the oven [Fig 3A] if there was a leak in the bottle, a plastic beaker was placed under the bottle and a slightly smaller plastic beaker was placed on top of it. The bottle was left in the oven at 95°C for 48h.

When the flask was taken out of the oven, the cap was not sufficiently closed because when the solution reaches 95°C the pressure loosens the cap and it needs to be retightened. There was also a small crack found on the bottom of the bottle at this time.

To be able to wash the catalyst, a large (18.5 cm) Büchner funnel was used. It was placed on a 1000 mL side-arm flask and a vacuum was generated with the help of a water ejector vacuum pump.

The catalyst from the bottle was poured into the funnel. The bottle was then refilled with distilled water to wash the catalyst in the funnel. In total the catalyst was washed with 4500 mL of distilled water. After it was washed thoroughly, the catalyst was left with suction for an extra 5 min to make sure that is was as dry as possible.

During and after the wash, some tests were done to see if the catalyst had formed well. The first indication of good formation was that some of the catalyst floated when it was washed. A second indication was that after the first litre of water had passed through the catalyst, the speed of water passing through increased a lot. These two observations indicate the presence of a porous product. Additionally, the still slightly wet catalyst felt spongy, which was a third indicator for a successful catalyst formation.

The filter paper with the catalyst was moved from the funnel by placing it upside down on a porcelain plate and blowing into the funnel. A spoon was used to remove the rest of the catalyst that remained in the funnel. The plate was placed in an oven set to 90°C and left there over night.

After Si-SBA-15 is dry, it should be avoided to inhale it. Therefore, all further work was preformed inside a fume cupboard. All catalyst was transferred to a mortar. To decrease the risk of making the catalyst electrostatic the work was done very slowly, which also reduced some loss of product since it easily flies away in the fuming cupboard if it is moved too fasts.

When the product had been transferred to the mortar, it was ground to a very fine powder. After that it was placed in a new 250 mL polyethylene bottle.

When calcining the catalyst there is some things to think about; first is to not take too much catalyst at the time because the risk of getting too much CO₂ in the air, which has a negative influence on the structure. Another thing is to not increase the
temperature too fast in the furnace [Fig 3C]; a good rate is $5^\circ$C/min so the furnace was set to take 1h and 20 min to increase from $0^\circ$C to $600^\circ$C, and then it was set to keep that temperature for 6h. To decrease the risk of having too much CO$_2$ in the air the circulation in the furnace was set to high. How to operate the furnace will be described under the heading: Using the furnace.

About 8g of catalyst (8.216g) was put in the furnace to be calcinated, the settings were made and the furnace was left over night. The following morning the weight of the calcinated product was measured to 4.216g.

**Tests of different niobium complexes**
To see if niobium ethoxide was able to hydrolyse slowly in different concentrations of HCl, small amounts of niobium ethoxide was added to diluted HCl (about 2M) and to 37% HCl.

NbCl$_5$ was tested as an alternative to niobium ethoxide. NbCl$_5$ are yellow crystals so they need to be dissolved before they are used. It was tested in distilled water, diluted and concentrated HCl and alcohol (according to research[15]).

Niobium oxalate, a white powder, was tested in water, diluted HCl and ethanol to see which would work.
Impregnation of 2, 5 and 10 wt% Nb on Si-SBA-15 using NbCl₅

<table>
<thead>
<tr>
<th>2g catalyst dissolved in 40 (5) ml ethanol (99.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Stir</td>
</tr>
<tr>
<td>Add correct amount of Nb dissolved in ethanol (99.5%)</td>
</tr>
<tr>
<td>1. Stir for 5 h</td>
</tr>
<tr>
<td>Evaporate ethanol by rotavapor</td>
</tr>
<tr>
<td>1.</td>
</tr>
<tr>
<td>Dry in oven at 100°C over night</td>
</tr>
<tr>
<td>1.</td>
</tr>
<tr>
<td>Calcinate at 600°C for 6h</td>
</tr>
</tbody>
</table>

Scheme 2: General procedure for impregnation, 40 ml used for SBA-15 and 5ml used for SiO₂

An overview of the procedure that will be presented below can be seen in scheme 2. To test how different amounts of niobium chloride impregnated on Si-SBA-15 differs in ability to oxidize α-pinene three different catalysts were made: 2, 5 and 10 wt% of NbCl₅.

To make these catalysts more than 6g of calcinated catalyst was needed, so almost all uncalcinated catalyst was put into the furnace for calcination. The catalyst was taken out of the furnace and used directly so there was no need to dry it extra.

The impregnation reactions don’t was done with NbCl₅ in ethanol.

To start preparing the impregnations three 100 mL round bottomed flasks were chosen for the reactions. Since the catalysts will stuck to the walls of the flasks when it dries and must be scraped off, flasks with wide necks were chooses to simplify the scraping.

In each flask 2g of dry Si-SBA-15 was weighed (2,006g 2,006g and 2,003g). After the catalyst was added it was dispersed in ethanol (99.5 %).

In the first flask 50 mL of ethanol was added, but that was too much liquid for that amount and type of catalyst. So in the other two flasks 40 mL of ethanol was added. The amount of ethanol used depends on the density and amount of catalyst, the goal is to have a good dispersion without it being too diluted.
Stirrers were then added to the flasks and put on stirring hot plates, glass stoppers were put on the flasks and they were left stirring for the time it took to do the NbCl$_5$ solution.

The total amount of NbCl$_5$ needed for all three impregnations were about 1.1g. 1.117g of NbCl$_5$ was weighed and added into a 50 mL standard measuring flask. Then some ethanol was poured into the flask to start the dilution. Some of the crystals are a little white on the surface (they should be yellow) and it didn’t dissolve, this is probably niobium that already has reacted with the water in the air. This decreases the amount of free Niobium in the solution, but the amount of reacted niobium is a lot less than the amount of dissolved niobium. The rest of the ethanol was added, up to the 50 mL mark and the flask was shaken well.

The calculations of how much Niobium that needs to be added for 2g catalyst to get 2, 5 and 10 wt% are calculated by:

\[
(1) \quad \text{amount of NbCl}_5 = \frac{\text{mole weight of NbCl}_5 \times \text{wt}\%}{\text{mole weight of Nb} \times (100-\text{wt}\%)} \times \text{amount of catalyst in g}
\]

The result for 2 wt% is 0.119g, for 5 wt% is 0.306g and for 10 wt% is 0.646g of NbCl$_5$.

And to calculate how many mL of solution that is needed to get the correct amount of Niobium is done by:

\[
(2) \quad \text{amount of solution} = \frac{50\text{mL ethanol} \times \text{amount of NbCl}_5 \text{needed in g}}{1.117g \text{ NbCl}_5}
\]

The result for 2 wt% is 5.33mL, for 5 wt% is 13.70mL and for 10 wt% is 28.92mL of NbCl$_5$ solution.

To add the correct amount of solution to the flasks a pipette with grades up to 10 mL with one decimal was used, to add the second decimal an auto pipette was used. The addition was made during stirring. The flask with 50 mL ethanol got the 2 wt% addition so the total amount of liquid would be as low as possible in the flasks.

The flasks were left stirring for 5h.

After 5h the ethanol was evaporated using a rotavapor. The water bath in the rotavapor was set to 70°C and the rotation speed was set quite high. The reason of using a rotavapor instead of putting it into the oven was to help spread out the amount of Niobium in the ethanol more evenly on the catalyst when the ethanol evaporates. That hopefully gave better catalytic properties.

After evaporation the flask was put into the oven over night at 100°C to evaporate the last of the ethanol.

After the flasks had dried over night, a bent spatula was used to get as much of the catalyst as possible out of the flask. The catalyst was then moved from the flask to a
mortar and it was grinded carefully. When all lumps were gone, the catalyst from the mortar to a small glass bottle for storage.

The catalysts were calcinated at 600°C, the temp increase time was 1h and 20 min and they were calcinated for 6h.

**Impregnation of 2, 5 and 10 wt% Nb on SiO₂ using NbCl₅**

An overview of the procedure that will be presented below can be seen in scheme 2. To compare how big difference the amount of surface area on a catalyst makes, the same kind of impregnation was made on dense SiO₂ with the same weight percentage as with Si-SBA-15.

The same principle of impregnation was used for SiO₂. 2.006g, 2.008g and 2.007g of dry SiO₂ was placed in each flask with a stirrer (same flasks and stirrers as before), and after that 5 mL of dry ethanol (99.5%) was poured into each flask.

The NbCl₅ solution was made in the same way as before but this time 1.121g of NbCl₅ was used. There was less amount of reacted Niobium this time which means that the concentration of Niobium was closer to the calculated amount.

The needed amount of NbCl₅ is the same as before but the amount of solution is different considering that the amount of dissolved Niobium is higher now.

\[
\text{amount of solution} = \frac{50 \text{mL ethanol} \times \text{amount of NbCl}_5 \text{ needed in g}}{1.121 \text{ g NbCl}_5} \tag{3}
\]

The amount of solution needed for 2 wt% is 5.31mL, for 5 wt% is 13.65mL and for 10 wt% is 28.81mL of NbCl₅ solution.

The catalysts were calcinated at 600°C, the temperature increase time was 1h and 20 min and they were calcinated for 6h.
Incorporation of niobium to Si-SBA-15 using niobium oxalate

Oil bath at 40°C

5g P123 dissolved in 37.5 ml distilled water
   ↓ Stir
Add 150 ml of 2 M HCl
   ↓ Stir for 3 h
Add 10.625g of TEOS (and niobium)
   ↓ Stir for 24h
Age in oven at 95°C for 48h
   ↓
Filter and wash with water
   ↓ (Stir with high pH niobium solution)
Dry over night in 100°C
   ↓
Calcinate at 600°C for 6h

Scheme 3: General procedure for producing Si/Nb-SBA-15. Adding niobium with TEOS is standard incorporation, adding niobium after washing is modified incorporation.

An overview of the procedure presented below can be seen in scheme 3. Preparing this catalyst will have the same basic procedure as Si-SBA-15, with a few changes.

5.003g P123 and 37.5 mL distilled water was added to a 500mL polyethylene bottle then a big stirrer was placed in the bottle.

150mL 2M HCl was made by mixing 125 mL distilled water and 25 mL 37% HCl (12M)

It was tested if Niobium oxalate was able to dissolve in TEOS but it wasn’t, so a water based solution was made with 1.371g Niobium-oxalate and as little water as possible to dissolve the powder.

10.627g of TEOS was added by plastic pipette and directly after the niobium solution was also added by plastic pipette. The niobium was added faster than the TEOS.

To wash the SBA-15, an appropriate sized Büchner funnel was chosen and the catalyst was washed with 2 litres of water. Then it was moved to a porcelain plate and dried in the oven over night at 100°C.

The catalyst was calcinated at 600°C, the temp increase time was 1h and 20 min and it was calcinated for 6h.
**Modified incorporation of niobium to Si-SBA-15 using niobium oxalate**

An overview of the procedure that will be presented below can be seen in scheme 3. Preparing this catalyst will have the same basic procedure as Si-SBA-15, with a few changes.

5.003g P123 and 37.5mL distilled water was added to a 500mL polyethylene bottle, and then a big stirrer was placed in the bottle.

150mL 2M HCl was made by mixing 125mL distilled water and 25 mL 37% HCl (12M)

10.626g of TEOS was added by plastic pipette.

The catalyst was in the oven for 44.5h instead of 48h.

To wash the catalyst an appropriate sized Büchner funnel was chosen and the catalyst was washed with 2 litres of water. Then the catalyst was placed on a plate and divided into smaller pieces and placed in a 250 mL round bottomed flask.

First 80 mL distilled water was added to the flask and then 1.372g of niobium oxalate diluted in 20 mL distilled water was poured into it. This mixture was stirred during the time it took to calibrate the pH meter in the range of 4.01 and 7.00 using buffer solutions. The reason for altering the pH is to make the dissolved niobium to hydrolyse. The pH was increased to pH 8 by addition of diluted ammonia. This diluted ammonia was made in a 50 mL measuring cylinder by 25 mL of distilled water and 25 mL ammonia up to the 50 mL mark. From this mixture 17 mL was used to make the pH go from pH 1.41 to pH 8.11.

This mixture was stirred for 2h with a glass stopper in the neck. After that the catalyst was washed the same way as before with 2 litres of distilled water. SBA-15 needs a low pH to remain its structure before calcinated, and because of this the structure collapsed a bit due to the high pH in the mixture. An indication of this is the increased amount of time it took to wash it. After the wash it was placed in the oven over night at 100°C.

After it was dried it had a yellowish colour but it went away during the grinding of the catalyst, then the catalyst was placed in a bottle for storage.

The catalyst was calcinated at 600°C, the temp increase time was 1h and 20 min and it was calcinated for 6h.
**Grafting niobium to Si-SBA-15 using niobium ethoxide**

\[
\begin{align*}
\text{Oil bath at 125°C} & \quad 2\text{g dry catalyst dissolved in 110 ml dry toluene} \\
& \quad \downarrow \text{Stir and remove all water with a Dean Stark apparatus} \\
\text{Oil bath at 110°C} & \quad \downarrow \text{Add correct amount of dissolved Nb} \\
& \quad \downarrow \text{Reflux for 5 h} \\
& \quad \downarrow \text{Wash with toluene} \\
& \quad \downarrow \text{Dry in oven at 100°C over night} \\
& \quad \downarrow \text{Calcinate at 600°C for 6h}
\end{align*}
\]

**Scheme 4: General procedure for grafting**

An overview of the procedure that will be presented below can be seen in scheme 4. To prepare the grafted Nb-SBA-15; 3g of calcinated Si-SBA-15 was dried in the oven for 22h in 100°C and then it was ground. 2.001g of dry catalyst was placed in a double necked 250 mL round bottom flask and then 110 mL of dry toluene was added to the flask.

A glass stopper was placed in one neck and a Dean Stark apparatus [Fig 3D] was attached to the other neck. The apparatus was used to remove the water from the catalyst and the toluene. It was done by placing the round bottomed flask in an oil bath and set the temperature to 125°C. To make sure that the toluene and water doesn't escape, a reflux condenser was placed on the Dean Stark apparatus. The apparatus was filled with dry toluene so when the mix of toluene and water evaporates from the flask up to the condenser and then cools down the water ended up at the bottom of the toluene reserve and the toluene at the top will go over the edge and end up in the flask so the distillation have a return flow of liquid.

After the water was removed from the flask the temperature was reduced to 110°C and 0.426 mL of niobium ethoxide was added by auto pipette when the temperature was 112°C. The amount of niobium was calculated to get the Si/Nb ratio to be 20. First the yield of calcinated SBA-15 was calculated by

\[
(4) \quad \frac{4.216\text{g calcinated cat}}{8.116\text{g uncalcinated cat}} \times 23.465\text{g tot uncalcinated cat} = 12.041\text{g cals catalyst}
\]

42.63g of TEOS gives 12.041g calcinated Si-SBA-15

~ 19 ~
To get the Si/Nb ratio the TEOS needs to be recalculated into mols

\[
\frac{42.61\,g\,TEOS}{208.33\,g\,TEOS/mole} = 0.2046\,mole
\]

To get the amount of niobium in mols needed

\[
\frac{0.1046\,moles\,of\,Si}{20} = 0.01023\,moles\,Nb
\]

To recalculate the amount into weight

\[
0.01023\,moles \times 318.21\,g/mole = 3.255\,g\,of\,niobium\,ethoxide
\]

But this is the amount of niobium for all SBA-15; it was recalculated for 2g of SBA-15

\[
\frac{3.255\,g\,Nb\,ethoxide}{12.842\,g\,SBA} \times 2\,g\,of\,SBA = 0.5407\,g\,Nb\,ethoxide
\]

Niobium ethoxide is a liquid and with the density the volume can be calculated

\[
\frac{0.5407\,g\,of\,Nb\,ethoxide}{1.263\,g\,Nb\,ethoxide/ml} = 0.426\,ml\,Nb\,ethoxide
\]

The mixture refluxed for 5h at 110°C and then was washed with toluene. A problem that occurred was that the catalyst was stuck on sides in the flask and did not go back into the solution until the flask had cooled down. The catalyst was dried over a weekend in 100°C.

After the catalyst was dry it was grinded and placed in a bottle until it was calcinated. The catalyst was calcinated again at 600°C, the temp increase time was 1h and 20 min and it was calcinated for 6h.
Testing catalysts
There are different types of procedures to test the catalysts; either in gas phase, in a pressure reactor or in a liquid phase. The one that was used in this case was the liquid phase.

The procedure that was used for most of the experiments was to stir 5 mmol of α-pinene, 10 mmol of peroxide and 10 mL of the solvent acetonitrile to a homogenous solution in a 25 mL double necked round bottomed flask with a stirrer.

After the liquids were stirred to a homogenous solution the 0.100g of dry catalyst was added and the flask was placed it in an oil bath at a specific temperature. All catalysts were dried at 100°C over night before being used. The flask was left for stirring with a reflux condenser in one of the necks and a septum in the other.

Aliquots of reaction mixture were withdrawn at different time intervals and analysed by a GC; the samples were filtered before injected into the chromatograph to prevent particles from getting into the GC.

Selecting peroxide
There were seven tests made for deciding what peroxide to use and how much. The reason for choosing TBHP as the primary peroxide was based on the article Ajaikumar et al. 2011 [16] where it was shown that the catalyst decomposes in H₂O₂. An overview of the results can be seen in table 1.

The first two tests were with 5 mmol 70% TBHP, 5 mmol α-pinene at 50°C and 70°C with 2 wt% SBA-15 as a catalyst. These reactions were left for 7h and samples were taken at 1, 2, 3 and 7h but it had very low conversion of 10% respective 15%.

Because of the low conversion the amount of peroxide was doubled to 10 mmol to see if it had any effect on the results. At the same time the catalysts and the temperature
were also modified. In the third reaction incorporated Nb-SBA-15 was used and in the fourth reaction 10 wt% Nb/SiO₂ was chosen. Both reactions were set to 90°C and these reactions were left for 24h. After 5h the conversion was at 2.6 and 1.1% respectively and after 24h the conversion for the incorporated Nb-SBA-15 was 16% and for the impregnated catalyst the results are missing.

A plausible reason for the low conversion could be that the peroxide was 3 years old but it had been kept in a fridge for that time. To test if the peroxide was too old a fifth reaction was set up with a known catalyst from [16] 3wt% Cu/TiO₂ that works well in this reaction setup with TBHP and 70°C. At the same time a sixth reaction with 30% H₂O₂ was tested to see if that performed better conversion than the other peroxide. This was tested with grafted Nb-SBA-15 at 50°C. The result from 3wt% Cu/TiO₂ was over 90% conversion with the old TBHP, so the peroxide seemed to work. In the other reaction with the grafted catalyst the conversion was about 60%. With these results the peroxide that was chosen was 30% H₂O₂.

For comparison a seventh reaction was made at 70°C, with 10 mmol H₂O₂ and 5 mmol α-pinene for 22h without any catalyst.

The GC-results from the first four reactions are difficult to compare to the rest because the settings on the GC wasn’t optimised yet.

**Testing temperature**

The best way of testing the catalyst would be to test all catalysts at all the seven temperatures, but there wasn’t time to do that so one catalyst was chosen to test the seven temperatures. The temperatures were room temperature¹, 40, 50, 60, 70, 80 and 90°C. The catalyst was the grafted Nb-SBA-15.

All the reactions were preformed in the same way; 10 mL of acetonitrile, 5 mmol of α-pinene, 10 mmol of H₂O₂ stirred to a homogenous solution, then 0.100g dry catalyst was added and the flask was placed in the oil bath at the set temperature.

All tests were taken at 1, 2, 4, 6 and 22h and the procedure was to stop the stirring 3 minutes before taking a sample and taking the sample from the top of the liquid to reduce the amount of catalyst getting stuck in the filter.

¹ The room temperature was approximately between 20-25°C. The inaccuracy is due to there was no thermometer measuring inside the fuming cabinet.
**Testing different catalysts**

The best temperature was chosen to be 40°C and this was based on the amount of converted α-pinene, the amount of byproducts and the selectivity of the products produced resulting from the temperature tests. The catalysts that were tested were 2, 5, 10 wt% of Nb on SiO₂, 2, 5, 10 wt% of Nb on SBA-15, incorporated SBA-15, modified incorporated SBA-15 and with no catalyst for reference. The grafted catalysts results were taken from the temperature study.

All the reactions were done in the same way; 10 mL of acetonitrile, 5 mmol of α-pinene, 10 mmol of H₂O₂ stirred to a homogenous solution, then 0.100g dry catalyst was added and the flask was placed in the oil bath at 40°C.

All tests were taken at 1, 2, 4, 6 and 22h and the procedure was to stop the stirring 3 minutes before taking a sample and taking the sample from the top of the liquid to reduce the amount of catalyst getting stuck in the filter.

**Settings for GC**

The gas chromatograph used in these experiments was Agilent Technologies, Model No. 7820A with a FID detector. It had a HP-PONA capillary column; 50 m long, 0.25 mm internal diameter and 0.2 µm film thickness. The GC had automatic split injection and used hydrogen as a carrier gas. The temperature programming was; Injection port temperature of 200°C, column temperature ranging from 70°C to 230°C with 1 minute holding time at the initial temperature and 8 minutes holding time at the final temperature, the heating ramp was set to 10°C/min.
RESULT AND DISCUSSION

Results from test of different niobium complexes
When testing if niobium ethoxide could hydrolyze slowly in diluted and concentrated HCl the results showed that that in both cases the niobium hydrolysed immediately. The conclusion were that niobium ethoxide required dry surroundings to hydrolyse slowly.

NbCl₅ was successfully dissolved in ethanol 99.5%. Some drops of water were added as a test which resulted that the NbCl₅ decomposed, i.e. NbCl₅ needs dry surroundings.

The niobium oxalate dissolved well in water and diluted HCl while it did not dissolve or decompose in ethanol.

Results from GC-MS
During the tests of the catalysts, samples were taken and run thought a GC with a special column; a HP-PONA capillary column. This was because the GC was used by others that needed that special column. The column worked well for separating the samples, but when some of the samples were run in the GC-MS to be able to identify the peaks from the GC a problem accrued. The separation column in the GC-MS was a HP-5 so the retention time was not the same as from the GC and could not be directly compared. Through elimination process the most likely products from the reactions are the ones listed below, but that is not 100% certain.

Results of the different peroxides
The results from these tests are difficult to compare because of the multiple variations in the procedure; temperature, catalyst, peroxide, peroxide:α-pinene ratio, measurements with good enough results at the same time and inconsistent GC-peaks because of altering with the times and temperatures.

To show the reason why H₂O₂ was preferred over TBHP for this reaction, four different settings were compared; the four are marked in blue in Table 1.

- 5 mmol TBHP, 2wt% Nb-SBA-15 at 70°C after 7h
- 10 mmol TBHP, 3wt.% Cu/TiO₂ [16] at 70°C after 6h
- 10 mmol H₂O₂, grafted Nb-SBA-15 at 50°C after 6h
- 10 mmol H₂O₂, no catalyst at 70°C after 6h.
3wt% Cu/TiO2 prepared by deposition precipitation method (not prepared in this project) and is perfected to be used for TBHP as peroxide in an oxidizing reaction of α-pinene. The conversion for this catalyst is very high after 6 h which indicates that the peroxide is working. The reaction with 2 wt% SBA-15 has a much lower conversion after 7h then the 3wt% Cu/TiO2 had after 6h. The third reaction was done without any catalyst and after 6h there was a higher conversion then in the second reaction. The H₂O₂ peroxide was tested a second time, now with a grafted catalyst at 50°C and after 6h the conversion was very high even though the temperature was lower than in the other tests.

**Results of the temperature study on grafted catalyst**

The results from the peroxide study with the grafted catalyst were very good; therefore the grafted catalyst was used for the temperature study. In the peroxide study the temperature was kept quite low at 50°C in the first test to see if the peroxide could cope with the temperature. The temperatures were increased gradually without problems up to 90°C, increasing the temperature higher was not of interest due to the diminishing increase in conversion. To get a complete temperature range two lower temperatures were tested as well.

The results of the conversion on all seven temperatures can be seen in Table 2 and Plot 1.
Table 2: The conversion of α-pinene at different times and temperatures

<table>
<thead>
<tr>
<th>Time</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp</td>
<td>3.2</td>
<td>4.4</td>
<td>9.0</td>
<td>12.1</td>
<td>25.9</td>
</tr>
<tr>
<td>40 °C</td>
<td>18.8</td>
<td>30.3</td>
<td>34.4</td>
<td>36.7</td>
<td>50.0</td>
</tr>
<tr>
<td>50 °C</td>
<td>40.1</td>
<td>44.1</td>
<td>49.4</td>
<td>61.1</td>
<td></td>
</tr>
<tr>
<td>60 °C</td>
<td>38.9</td>
<td>41.8</td>
<td>54.0</td>
<td>48.7</td>
<td>72.7</td>
</tr>
<tr>
<td>70 °C</td>
<td>48.3</td>
<td>56.6</td>
<td>61.2</td>
<td>67.1</td>
<td>83.4</td>
</tr>
<tr>
<td>80 °C</td>
<td>50.2</td>
<td>55.3</td>
<td>62.7</td>
<td>70.5</td>
<td>84.9</td>
</tr>
<tr>
<td>90 °C</td>
<td>50.5</td>
<td>48.2</td>
<td>54.9</td>
<td>60.5</td>
<td>87.7</td>
</tr>
</tbody>
</table>

Effect of Temperatures on Conversion of α-Pinene

Plot 1: This is the plot of Table 2.

Plot 1 clearly shows that there is a correlation between temperature and conversion up to about 70°C, after that the conversion is about constant for 70, 80 and 90°C. A good catalyst should give good conversion but it also needs to give high selectivity. In this report the focus has been to get high selectivity. Nine products has been chosen to be main products for the temperature study, the rest are byproducts.

Table 3: The table displays the distribution in percentage of products for all temperatures after 2h.

<table>
<thead>
<tr>
<th>2h</th>
<th>Room Temp</th>
<th>40 °C</th>
<th>50 °C</th>
<th>60 °C</th>
<th>70 °C</th>
<th>80 °C</th>
<th>90 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campholenic aldehydes</td>
<td>20.3</td>
<td>9.8</td>
<td>10.9</td>
<td>9.7</td>
<td>7.8</td>
<td>8.9</td>
<td>10.6</td>
</tr>
<tr>
<td>verbenol</td>
<td>9.0</td>
<td>3.0</td>
<td>4.4</td>
<td>3.5</td>
<td>4.3</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Verbenone</td>
<td>6.2</td>
<td>1.3</td>
<td>1.9</td>
<td>2.2</td>
<td>3.0</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Pinanediol</td>
<td>0.0</td>
<td>2.8</td>
<td>7.8</td>
<td>6.3</td>
<td>4.1</td>
<td>6.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Unknown prod1</td>
<td>10.9</td>
<td>9.2</td>
<td>5.7</td>
<td>5.8</td>
<td>2.5</td>
<td>2.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Pinocarveol</td>
<td>18.5</td>
<td>32.7</td>
<td>22.6</td>
<td>24.5</td>
<td>14.9</td>
<td>22.3</td>
<td>22.9</td>
</tr>
<tr>
<td>Unknown prod2</td>
<td>0.0</td>
<td>3.9</td>
<td>6.7</td>
<td>7.3</td>
<td>5.8</td>
<td>8.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Cymenol</td>
<td>10.4</td>
<td>3.9</td>
<td>9.6</td>
<td>9.2</td>
<td>8.6</td>
<td>9.4</td>
<td>9.0</td>
</tr>
<tr>
<td>Oligomerized Product</td>
<td>14.1</td>
<td>9.8</td>
<td>12.7</td>
<td>10.7</td>
<td>9.4</td>
<td>9.6</td>
<td>9.9</td>
</tr>
<tr>
<td>Byproduct</td>
<td>10.5</td>
<td>19.9</td>
<td>17.9</td>
<td>20.9</td>
<td>39.6</td>
<td>26.1</td>
<td>26.6</td>
</tr>
<tr>
<td>Conversion</td>
<td>4.39</td>
<td>30.32</td>
<td>40.08</td>
<td>41.75</td>
<td>56.64</td>
<td>55.26</td>
<td>48.20</td>
</tr>
</tbody>
</table>
After the first two hours the reaction is quite selective towards pinocarveol, but there is only a low amount conversion. There need to be a balance between the amount of product produced and the selectivity.

Table 4: This table displays the distribution in % of products for all temperatures after 22h.

<table>
<thead>
<tr>
<th>22h</th>
<th>Room Temp</th>
<th>40 °C</th>
<th>50 °C</th>
<th>60 °C</th>
<th>70 °C</th>
<th>80 °C</th>
<th>90 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campholenic aldehydes</td>
<td>11,8</td>
<td>8,0</td>
<td>7,4</td>
<td>4,9</td>
<td>4,7</td>
<td>5,0</td>
<td>8,4</td>
</tr>
<tr>
<td>verbenol</td>
<td>2,9</td>
<td>3,2</td>
<td>3,9</td>
<td>4,1</td>
<td>7,4</td>
<td>7,4</td>
<td>10,2</td>
</tr>
<tr>
<td>Verbenone</td>
<td>0,0</td>
<td>2,0</td>
<td>2,7</td>
<td>3,7</td>
<td>6,4</td>
<td>5,7</td>
<td>5,2</td>
</tr>
<tr>
<td>Pinanediol</td>
<td>4,3</td>
<td>5,1</td>
<td>6,6</td>
<td>4,4</td>
<td>3,9</td>
<td>5,5</td>
<td>2,9</td>
</tr>
<tr>
<td>Unknown prod1</td>
<td>5,9</td>
<td>9,1</td>
<td>4,8</td>
<td>2,4</td>
<td>0,0</td>
<td>0,5</td>
<td>0,6</td>
</tr>
<tr>
<td>Pinocarveol</td>
<td>35,0</td>
<td>25,7</td>
<td>18,0</td>
<td>15,4</td>
<td>9,8</td>
<td>11,5</td>
<td>8,2</td>
</tr>
<tr>
<td>Unknown prod2</td>
<td>6,5</td>
<td>9,5</td>
<td>9,2</td>
<td>7,9</td>
<td>7,0</td>
<td>7,9</td>
<td>4,3</td>
</tr>
<tr>
<td>Cymenol</td>
<td>8,6</td>
<td>7,3</td>
<td>7,8</td>
<td>7,3</td>
<td>8,5</td>
<td>8,0</td>
<td>6,8</td>
</tr>
<tr>
<td>Oligomerized Product</td>
<td>13,2</td>
<td>9,0</td>
<td>10,2</td>
<td>8,4</td>
<td>10,2</td>
<td>8,9</td>
<td>6,7</td>
</tr>
<tr>
<td>Byproduct</td>
<td>11,7</td>
<td>21,1</td>
<td>29,5</td>
<td>41,5</td>
<td>42,3</td>
<td>39,7</td>
<td>46,7</td>
</tr>
<tr>
<td>Conversion</td>
<td>25.85</td>
<td>50.01</td>
<td>61.11</td>
<td>72.73</td>
<td>83.43</td>
<td>84.91</td>
<td>87.68</td>
</tr>
</tbody>
</table>

Plot 3: This is a plot of Table 4.
After 22h the results have changed which can be seen if plot 2 and 3 are compared; in the higher temperatures the amount of byproduct has taken over and the amount of pinocarveol is equal with the rest of the products, meanwhile for the lower temperatures the amount of byproducts are not that high compared to the amount of pinocarveol.

The selectivity was the main factor in this project which excludes reactions of 50 - 90°C because of the high amounts of byproduct. If the conversion and time are taken into consideration the room temperature reaction is not reactive enough though the 40°C reaction had a higher conversion after 2h than the room temperature reaction had after 22h. Deciding the amount of time to run the reaction was based on: the time, amount of Pinanediol, conversion and byproduct. From Table 5 the decision was to run the following reactions at 40°C for 22h.

**Table 5**: Shows the relation between time and products. The best scenario is short time, high conversion, high amount of Pinanediol and low byproduct

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Pinocarveol (%)</th>
<th>α-pinene conversion (%)</th>
<th>Byproduct (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32,2</td>
<td>18,8</td>
<td>16,3</td>
</tr>
<tr>
<td>2</td>
<td>32,7</td>
<td>30,3</td>
<td>19,9</td>
</tr>
<tr>
<td>4</td>
<td>31,0</td>
<td>34,4</td>
<td>16,0</td>
</tr>
<tr>
<td>6</td>
<td>30,4</td>
<td>36,7</td>
<td>15,8</td>
</tr>
<tr>
<td>22</td>
<td>25,7</td>
<td>50,0</td>
<td>21,1</td>
</tr>
</tbody>
</table>

**The activity of different catalysts on oxidation of α-pinene at 40°C**

After the temperature tests on grafted Nb-SBA-15 the same type of reaction was made on the rest of the catalysts. The conversion over time can be seen in Table 6 and Plot 4.

**Table 6**: Shows the percentage of converted α-pinene for each catalyst over time.

<table>
<thead>
<tr>
<th>Time</th>
<th>1 h</th>
<th>2 h</th>
<th>4 h</th>
<th>6 h</th>
<th>22 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-SBA-15 (grafted)</td>
<td>18,8</td>
<td>30,3</td>
<td>34,4</td>
<td>36,7</td>
<td>50,0</td>
</tr>
<tr>
<td>2wt.% Nb/SBA-15</td>
<td>8,8</td>
<td>13,5</td>
<td>26,8</td>
<td>24,6</td>
<td>43,7</td>
</tr>
<tr>
<td>5wt.% Nb/SBA-15</td>
<td>18,1</td>
<td>23,9</td>
<td>32,6</td>
<td>34,4</td>
<td>46,5</td>
</tr>
<tr>
<td>10wt.% Nb/SBA-15</td>
<td>14,0</td>
<td>21,7</td>
<td>30,6</td>
<td>32,2</td>
<td>45,5</td>
</tr>
<tr>
<td>Nb-Sba-15 (mod incorp)</td>
<td>18,1</td>
<td>24,3</td>
<td>28,2</td>
<td>31,5</td>
<td>38,9</td>
</tr>
<tr>
<td>Nb-Sba-15 (Incorp)</td>
<td>2,1</td>
<td>3,7</td>
<td>5,6</td>
<td>7,1</td>
<td>14,0</td>
</tr>
<tr>
<td>2wt.% Nb/SiO2</td>
<td>0,5</td>
<td>0,8</td>
<td>2,3</td>
<td>3,8</td>
<td>14,8</td>
</tr>
<tr>
<td>5wt.% Nb/SiO2</td>
<td>2,2</td>
<td>3,3</td>
<td>7,4</td>
<td>10,1</td>
<td>34,3</td>
</tr>
<tr>
<td>10wt.% Nb/SiO2</td>
<td>0,5</td>
<td>0,5</td>
<td>2,2</td>
<td>4,5</td>
<td>24,3</td>
</tr>
<tr>
<td>No Catalyst</td>
<td>0,5</td>
<td>0,8</td>
<td>0,9</td>
<td>0,5</td>
<td>11,3</td>
</tr>
</tbody>
</table>
**Plot 4:** This is a plot of Table 6 with the conversion for all catalysts over time.

The statements below are referred to 40°C only; if the tests were made in different temperatures like in the temperature study then the results would be more reliable.

In plot 4 there are quite clear groupings with;

1. No catalyst, the three Nb-SiO₂ catalysts and modified incorporated Nb-SBA-15.
2. The grafted Nb-SBA-15, the three impregnated Nb-SBA-15 and the incorporated Nb-SBA-15.

In the first group the reaction without catalyst had the lowest conversion yield but very close to that was the incorporated Nb-SBA-15 with almost the same amount of conversion. When the catalyst was prepared the structure seemed to have formed well but from that data in Table 6 the likelihood of any amount of Niobium being incorporated into the SBA-15 structure is very low if it is compared to the conversion rate of the other Nb-SBA-15, no matter the amount of Niobium on them. To be certain about how well the Nb-SBA-15 structure was formed it needs to be characterised. A possibility to improve the catalyst could be to test other pH levels while adding the niobium to help to incorporate it into the structure.

By comparing the three different impregnated Nb/SiO₂ shows clearly that the highest amount of niobium might not give the best results according to plot 4. The fact that 5 wt% Nb/SiO₂ has an amount of conversion that is closer to the modified Nb-SBA-15’s amount and the rest of the higher group than the 2wt% and 10wt% Nb/SiO₂ point towards that higher amounts of niobium doesn’t produce more conversion.

The three impregnated Nb-SBA-15 show the same tendency; the 5wt% is the best and then the 10wt% and last the 2wt%, which suggests that the sweet spot is between 2 and 10 and close to 5wt%. Comparing the two supports it is clear that the SBA-15 produces higher conversion than the SiO₂ no matter the wt% of niobium loaded on to it.
The modified incorporated catalyst gives a quite high conversion considering that the structure collapsed a bit during the preparation when it was stirred in a high pH solution, before it was calcinated, in an attempt to incorporate niobium into the structure. The method seems to have worked on some level, since it had a lot better conversion than the incorporated Nb-SBA-15. The method could probably be perfected by finding the optimum pH and time to stir the catalyst in the niobium solution to reduce the structure collapse and find the best amount of niobium suited for this catalyst.

The grafted Nb-SBA-15 is obviously the one with the highest conversion considering that the reaction is based on its optimum reaction. The fact that the amount of niobium on the grafted catalyst is unknown, it would be good to characterize it to see the result. Another aspect of improving this catalyst could be to vary the amount of niobium on the catalyst to see if the results changes.

An interesting fact is that all the impregnated Nb-SBA-15 catalysts are very close to the grafted catalysts level of conversion is interesting and it could be an idea to look into. Especially that they might have a better optimum then 5wt% and that they need another temperature to get the best results.

The results in Table 7 and 8 with the Plots 6, 7 and 8 shows the ten main products and the amount of byproducts produced during the tests of all the catalysts.

Table 7: Shows the distribution of products in % for each catalyst after 2h. The products are:
1-Pinene oxide, 2-Campholenic aldehydes, 3-Verbenol, 4-Verbinon, 5-Pinanediol, 6-Unknown product 1, 7-Pinocarveol, 8-Unknown product 2, 9-Cymenol, 10-Oligomerized product, 11-Byproduct, 12-Conversion

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Table 8: Shows the distribution of products in % for each catalyst after 22h. The products are:
1-Pinene oxide, 2-Campholenic aldehydes, 3-Verbenol, 4-Verbinon, 5-Pinanediol,
6-Unknown product 1, 7-Pinocarveol, 8-Unknown product 2, 9-Cymenol, 10-Oligomerized product, 11-Byproduct, 12-Conversion

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<td>11,3</td>
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</table>

Plot 6: This is a plot of Table 8
Table 7 and plot 5 shows the distribution of products for each reaction after 2h. The two groups that were mentioned earlier are even clearer here, considering that the second group has some product when the first group has none after 2h.

Table 8 and Plot 6 show the distribution of products for each reaction after 22h. The group of catalysts with high conversion give more byproducts and less pinocarveol than the catalyst with lower conversion except for the incorporated SBA-15 that gives low conversion but gives both low byproducts and low pinocarveol. So the lower group is more selective but doesn’t give as much product.

The two unknown products were very close to the pinocarveol; unknown 1 at 13.15 min, pinocarveol at 13.29 min and unknown 2 at 13.45 min on the GC spectra so they could be isomers of pinocarveol. If that would be the case the selectivity would be even higher for pinocarveol.

Pinocarveol is an expensive substance that can be bought at Sigma Aldrich for 763.83 kr, which will give you a 1 mL flask with ≥96.0% purity compared with the raw material 98% pure α-pinene in a 250 mL bottle that was bought for 736.92 kr. If it was possible to improve a catalyst to produce 96% pure pinocarveol the profit would almost be 250 times the money for the raw product, before the cost of producing the pinocarveol.[17,18]
CONCLUSIONS

The conclusions drawn from this project are:

- Niobium on silica works as a catalyst for oxidising α-pinene.
- Nb-SBA-15 works with H₂O₂ 30wt%, which is environmentally friendly chemical substance.
- The reaction between H₂O₂ and α-pinene produces pinocarveol as the major product, instead of the usual products; verbenol, verbenone, pinene oxide and campholenic aldehydes.
- The impregnated Nb-SBA-15 catalysts give better conversion than the impregnated SiO₂.
- The best catalyst made in this project was the grafted one when it was used at 40°C.
- Using SBA-15 as the support of the catalyst works well and could be a good subject for future research.

OUTLOOK

This project was only a small testing period and to see if there is a point to move on and explore the area more or if it wouldn’t work. The results show that it does work, though more research is needed to get more data and to improve the catalysts.

Things that need to be addressed to confirm some of the things in the discussion are:

- Test all temperatures and times for all catalysts to get a better understanding of how they react to temperature differences.
- Do characterization tests on the catalysts to see if the structure has formed well and how the niobium is spread out on the surface.
- Test if addition of gold or other metals on the catalysts together with the niobium improves the results.
- Do changes on the incorporated, modified incorporated and grafted catalyst by changing pH during the procedure and change the Si/Nb ratio both by increase and decrease the amount of niobium.
- Test out the optimum amount of niobium for the impregnation method.
- Evaluate if the reaction can be done in a more eco friendly solvent.

ACKNOWLEDGEMENT

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REFERENCES


[13] O.S. University, GC-MS.


