

The effects of alkali promotion on silver catalysts for the epoxidation of ethylene

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1. Abstract

Ethylene oxide is one of the most produced compounds in the petrochemical industry. It is a versatile chemical compound mostly used in the synthesis of ethylene glycol, which is used to produce antifreezing agents and plastics. Ethylene oxide is synthesized by the epoxidation of ethylene. This occurs over a silver catalyst, supported on an α -alumina carrier.

In industry, these catalysts are promoted with cesium to enhance their selectivity towards ethylene oxide. On the other alkali metals, not many experimental research has been carried out. Therefore in this project, the effects of alkali promotion on the catalytic performance of supported silver catalysts are investigated for the epoxidation of ethylene.

The alkali metals used are sodium, potassium, rubidium and cesium. The catalysts are synthesized by co-impregnating the silver and the alkali promoter on the α -alumina via an incipient wetness impregnation. The catalysts had a target weight loading of 15 wt% silver and different amounts of alkali promoter, ranging from 0 to 0.08 mol%. ICP was performed to determine the exact weight loading and the silver particle size was measured from SEM images.

The catalysts were tested in an epoxidation setup, while ethyl chloride was added in 0-1.8 ppm concentrations to the reaction feed.

First, it was found that increasing the ethyl chloride concentration from 0 to 0.9 to 1.8 ppm led to an increase in selectivity, while having a decrease in conversion. Secondly, when promoting the catalyst with the alkali promoters, it showed a decrease in selectivity for all the alkali's except rubidium. The rubidium catalyst showed a selectivity comparable to the unpromoted catalyst. Third, the weight loading of cesium was changed to look at the effect of differences in weight loading. It showed a decrease in selectivity when increasing the amount of cesium promoter. Last of all, a cesium catalyst was prepared with a cesium carbonate precursor instead of the hydroxide to check whether it would have an effect on the catalytic performance. The catalyst prepared with the carbonate precursor showed both a higher conversion and selectivity.

2. Layman's abstract

Ethylene oxide is a chemical compound that is widely used for the production of many every-day products. It is used for the production of antifreezing agents, isolation foams and plastic bottles and packaging. In order to produce this ethylene oxide with the least amount of energy and the least amount of side products, a catalyst is used in the reaction.

A catalyst is a substance that can speed up a chemical reaction by lowering the activation energy of the reaction. The catalyst creates a path to the end product of the reaction that costs less energy and is easier to take.

Almost every reaction needs their own catalyst. In this project, the catalyst consists of silver particles. These silver particles alone are not stable and they are therefore deposited on a support material. The support material of the catalyst for this reaction is aluminium oxide.

In order to improve the catalysts, they are promoted with small amounts of others elements. This can increase the yield of the reaction, the stability of the catalyst and the selectivity of the desired end product. In this project, the aluminium oxide supported silver catalysts are promoted with alkali promoters to see if they can increase the selectivity. The alkali metals are the first group of the periodic table and consist of lithium, sodium, potassium, rubidium, cesium and francium. Here, only the effects of sodium, potassium, rubidium and cesium will be studied.

3. Introduction

The epoxidation of ethylene to ethylene oxide is an important large-scale industrial process. The production is expected to reach around 32 megatonnes per year worldwide at the end of 2023.¹ Ethylene oxide has a strained ring, making it a very reactive chemical. Because of this high reactivity, it serves as a very useful and versatile chemical intermediate. Ethylene oxide itself can be used as a disinfectant and sterilizing agent², but most of the ethylene oxide will be made into ethylene glycols. These are chemicals that are used in antifreezing agents or will be turned into polyesters and plastics, for bottles and food packaging, and polyurethanes, for isolation foams.

The epoxidation of ethylene occurs over a silver catalyst on an alumina support material. There are several reactions that take place on this catalyst. First, the ethylene gets converted on the silver particles to the desired ethylene oxide and the undesired acetaldehyde. The produced ethylene oxide can then isomerize into acetaldehyde over the hydroxyl groups of the support. Finally, the acetaldehyde is turned into CO₂ and H₂O over the silver particles by total combustion.

One way to increase the selectivity is to suppress the isomerization of ethylene oxide by limiting the amount of hydroxyl groups. That is the reason why α -alumina is the preferred support material for this reaction. α -alumina has a low specific surface area and a low hydroxyl group density. Combining these two properties gives an overall low amount of hydroxyl groups on the support material.³ Catalysts with silver on α -alumina show a selectivity of around 50%.

In industry, the catalysts are also promoted with cesium to increase the selectivity. The promotion of the catalyst with cesium leads to an increase in the selectivity from 50% to around 90%.^{4,3} The exact mechanism of how cesium increases the selectivity is still in debate, but it is suggested that cesium inhibits the hydroxyl groups of the support material, thereby limiting the degree of isomerization.⁵ Another suggested theory is that cesium increases the electrophilicity of the atomic oxygen, making it easier to open up the ethylene double bond and form the epoxide ring.⁶

The effect of the promotion with other alkali promoters on the selectivity of the reaction has been studied in some DFT studies^{6,7}, but no real experimental research has been conducted. In this project, the effects of alkali promotion on the silver catalysts on the selectivity of the epoxidation reaction of ethylene will be studied.

4. Theoretical background

This chapter explains the theoretical background of this thesis topic. The mechanism of the reaction and the function of the catalyst are explained. Furthermore, the effect of promotion on the catalysts is explained. Finally, some techniques that will be used are described.

4.1 Mechanism of ethylene epoxidation

The selective oxidation of ethylene is catalyzed by a silver catalyst on an aluminium oxide (alumina, Al_2O_3) support material. A schematic overview of the reaction mechanism is given in Figure 1. On these silver particles, ethylene can be turned into ethylene oxide (EO), which is the selective pathway to the desired product (k_1). However, the ethylene can also be turned into CO_2 and H_2O over the silver particles, which is the non-selective pathway to the undesired product (k_2).

The EO can on its turn be combusted into CO_2 and H_2O (k_3) over the hydroxyl groups of the support material.^{8,9}

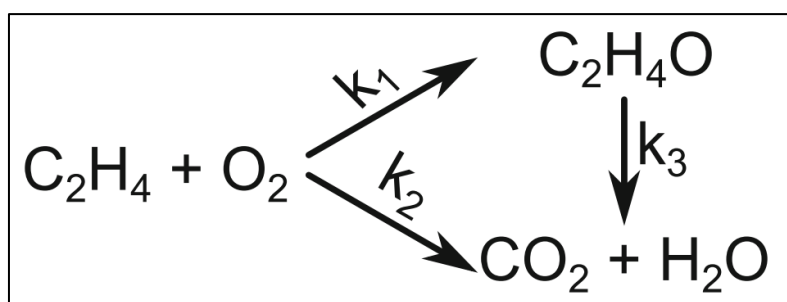
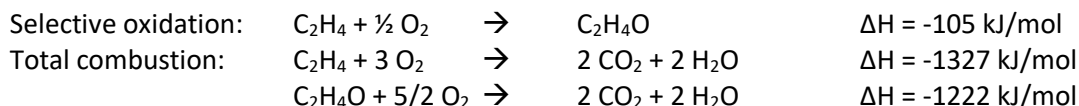


Figure 1. Reaction scheme for the ethylene epoxidation. k_1 shows the selective oxidation of ethylene to EO. k_2 shows the non-selective oxidation of ethylene to CO_2 and H_2O . k_3 is the combustion reaction of EO to CO_2 and water.⁸

Reaching high selectivity towards EO is difficult because the side reactions are highly thermodynamically favored. Where the desired formation of EO is just slightly exothermic, the total combustions of ethylene and EO are strongly exothermic.¹⁰



It was first believed that the oxygen species that is responsible for the selective oxidation of ethylene was molecular oxygen, adsorbed to the silver surface.¹¹

Later it was found not to be this molecular oxygen species, but an atomic adsorbed oxygen that caused the selective oxidation reaction.^{11,12,13} In addition, it was stated that this atomic oxygen could be either electrophilic or nucleophilic.¹⁴ The electrophilic oxygen is weakly bound to the silver surface and is responsible for the selective oxidation of ethylene via an Eley-Rideal mechanism. The $\text{C}=\text{C}$ double bond of ethylene attacks the electrophilic oxygen. This opens up the double bond, where the oxygen gets inserted and a $\text{C}-\text{O}-\text{C}$ ring is formed, which leads to the formation of EO.

The nucleophilic oxygen is strongly bound to the silver surface and is responsible for the non-selective oxidation of ethylene via a Langmuir-Hinshelwood mechanism. The oxygen attacks the $\text{C}-\text{H}$ bond of the ethylene, thereby removing a hydrogen atom. This leaves a radical molecule, which will completely combust into CO_2 and H_2O .⁸

4.2 Oxometallacycle intermediate

After this epoxidation mechanism was proposed, an oxometallacycle (OMC) surface intermediate was discovered with DFT calculations by Linic and Barteau.^{15,16} In this newly found OMC mechanism, which

is shown in Figure 2, both the atomic oxygen and the ethylene adsorb to the silver surface. There they react via a Langmuir-Hinshelwood mechanism to form the OMC surface intermediate (r_1).

The OMC surface intermediate can then be turned into EO via the selective oxidation (r_2), but it can also form acetaldehyde (AA) via the total oxidation (r_3). The EO is able to isomerize into AA (r_5) over the hydroxyl groups and the AA will be combusted into CO_2 and H_2O over the silver particles.

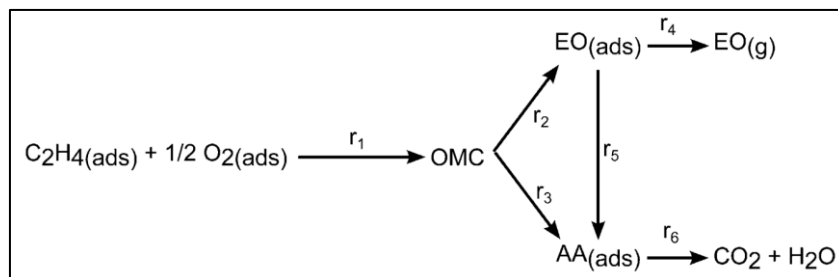


Figure 2. The OMC mechanism.⁵

In this mechanism, the OMC intermediate reacts via ring closure to form the ethylene oxide. Acetaldehyde is formed via hydrogen transfer. The relative activation barriers of EO and AA determine the product selectivity.

4.3 Alumina support material

In heterogeneous catalysis, it is most often small metal particles that are the active sites for the catalytic reaction. Unfortunately, these particles are unstable and susceptible to sintering. In order to stabilize the particles and protect them from sintering, they are deposited on a support material. Alumina is the support material most widely used in catalysis, because of its high thermal and mechanical stability.

There are several phases which alumina can adopt, but three phases are used most often. The η - and γ -alumina, which are both porous and amorphous, and the α -alumina, which is nonporous and has a crystalline structure. The nonporosity of the α -alumina leads to a low specific surface area and results in a low amount of hydroxyl groups on the support. These hydroxyl groups catalyze the isomerization of ethylene oxide into acetaldehyde, which is undesired. The α -alumina makes therefore the best support material for the selective oxidation of ethylene to ethylene oxide.¹⁷

4.4 Silver as catalyst

As stated before, it is now generally believed to be atomic oxygen that is the active oxygen species for the selective oxidation of ethylene. To obtain this atomic oxygen, the catalyst should be able to dissociate molecular oxygen.^{12,13} Besides this ability, the bond strength of the atomic oxygen to the metal should be weak enough for the selective oxidation to take place.

This makes silver the most widely used and most efficient catalyst for ethylene epoxidation, in terms of selectivity. This is because silver is strong enough to dissociate the molecular oxygen and weak enough not to break the C-H bond, which would lead to the non-selective oxidation. The oxygen is relatively weakly bound to the silver surface, which makes it possible to react with the ethylene and form ethylene oxide.¹⁴ Other transition metals give complete combustion of ethylene, because they activate the C-H bonds too easily.¹⁸ In the ethylene epoxidation reaction, the C-H bond does get activated by the atomic oxygen, but compared to the insertion of oxygen into the ethylene double bond, this reaction is slow.¹⁴

Besides this, there have been studies on the oxide surfaces being the active phase for the selective oxidation. Özbek et al¹⁸ conducted a DFT study on the metal oxide surfaces $\text{Ag}_2\text{O}(001)$, $\text{Au}_2\text{O}(001)$ and $\text{Cu}_2\text{O}(001)$. $\text{Au}_2\text{O}(001)$ was found to be not a stable structure. The formed OMC intermediate reacts back to adsorbed ethylene, since it has a lower activation barrier than Au_2O . Cu_2O showed a very low

selectivity towards EO formation, because of the high EO desorption energy and a weak C-O bond. This causes the non-selective AA formation to compete with the EO formation and results in the low EO selectivity. Ag₂O being more stable than Au₂O and having a stronger C-O bond than Cu₂O confirms that silver catalysts are the most efficient and unique catalysts for the epoxidation of ethylene.¹⁸

While it was first believed that the silver particle size influences the selectivity of the catalyst towards EO, van den Reijen et al.³ recently found that the selectivity is particle size independent and it is actually the activity that is influenced by the particle size, since the selectivity decreases with increasing ethylene conversion. They showed that the turnover frequency (TOF) increased linearly with increasing particle size up to 60 nm, where the TOF was no longer dependent on the silver particle size.

4.5 Promoters

Promoters are added to the catalyst to enhance its catalytic performance. In the case of ethylene epoxidation, they are specifically added to enhance the selectivity towards ethylene oxide. Known promoters are cesium, chlorine, rhenium and molybdenum. Cesium and chlorine are the promoters studied most extensively and are the promoters relevant for this research, together with the other alkali metals. Therefore, only their effects will be discussed in this section.

4.5.1 Cesium and other alkali metals

In industry, silver catalysts are typically promoted with cesium. The addition of cesium is known to have a negative effect on the activity of the silver catalyst.

However, cesium does enhance the selectivity of the silver catalyst. The exact mechanism is still in debate, but several explanations have been proposed. It is suggested that cesium inhibits the hydroxyl groups on the alumina support material that isomerize ethylene oxide to acetaldehyde.^{5,19} Another reason could be that cesium acts as a binder between the silver and the alumina, leading to a better binding and dispersion of the silver particles on the support.¹⁹ In addition, it is believed that cesium interacts with silver and lowers the binding strength of EO to the silver surface, thereby limiting the combustion of EO, leading to less formation of carbon dioxide.^{10,20}

Besides the experimental studies on the effect of cesium promotion on the epoxidation of ethylene, DFT studies have been conducted. In these studies, calculations showed that alkali promoters stabilize the transition state for EO formation compared to the transition state for AA formation. This is done by increasing the activation barrier for AA formation more than the activation barrier for EO formation. The alkali promoters change the energies of these transition states due to the electric effects of their electronegativity. They induce a dipole on the surface and increase the selectivity.

This is the reason why cesium is the most effective alkali metal for promotion. With the lowest electronegativity, it is able to induce the largest charge difference and dipole field.⁶

DFT calculations also showed that the promotion of the catalyst with cesium weakens the adsorption of atomic oxygen on the silver surface, which lowers the electron density of the atomic oxygen adsorbed on the silver surface. This enhances the electrophilic attack of the atomic oxygen at the C=C bond of ethylene, because of the high electron density in the π -bond of the ethylene double bond. This way, the addition of cesium results in a higher EO selectivity, because it lowers the activation energy for the formation of the oxometallacycle and EO and increases the activation barrier for AA.⁶ Hence, the selectivity can be shifted by manipulating the dipole moment with the addition of ionic promoters.²¹

4.5.2 Chlorine

Whereas the alkali are added as solid promoters, it is also possible to add a gaseous promoter during catalysis. The chlorine is added in ppm amounts to the reaction feed as chlorinated hydrocarbons, such as ethyl chloride and vinyl chloride. The chlorine is deposited on the catalyst surface by combustion of

the hydrocarbon part. To prevent accumulation of chlorine, which acts as a poison for the catalyst, the chlorine is stripped away by the ethylene in the reaction feed.²¹

Chlorine increases the ethylene oxide selectivity at the cost of a strong decrease in activity.²² Chlorine, however, promotes the catalyst in a different way than the alkali promoters do, since it is strongly electronegative compared to the electropositive alkali metals.

The surface chlorine blocks oxygen vacant sites on the silver surface. This forces ethylene to not being able to bond to the silver surface. In this way, the ethylene stays in the gas phase and reacts with the adsorbed oxygen via the Eley-Rideal mechanism. This mechanism favors the selective oxidation of ethylene and increases the selectivity towards ethylene oxide.²³

With chlorine on the silver surface, there is less space for oxygen to adsorb. This explains the decrease in activity upon promotion with chlorine.²³

Chlorine also reduces the charge on the atomic oxygen, making it more electrophilic and susceptible towards the selective pathway.²⁴

4.6 Preparation and characterization techniques

Here, the catalyst preparation technique and the techniques that will be used to characterize the catalyst are described.

4.6.1 Incipient Wetness Impregnation

There are several ways to get the active metal particle on the support material. One of these ways is by incipient wetness impregnation. With this method, the metal precursor is dissolved in an impregnation solution. The impregnation solution is added to your dried support material, where the amount of impregnation solution is the same as the pore volume of your support. The solution will go into the pores by a capillary effect.

The catalyst will then be dried to evaporate the impregnation solution and subsequently be calcined to burn off any potential organic compounds. After the calcination, the metal is deposited on the support material.²⁵

4.6.2 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a microscope that, unlike a light microscope, uses electrons to form an image. Electrons have a smaller wavelength than photons and therefore give rise to an increased resolution. These electrons are produced as a beam by an electron gun at the top of the microscope. They are directed down the microscope, under vacuum, and are focused by several magnetic lenses. When the beam hits the sample, X-rays, backscattered electrons and secondary electrons are ejected from the sample. These electrons are detected and converted into a signal. The electron beam is rastered across the surface of the sample and all these different signals together construct the final SEM image. SEM can be used to acquire more information about particle sizes, interparticle distance and homogeneity of the particles on the support material.²⁶

4.6.3 Transmission Electron Microscopy

A transmission electron microscope (TEM) is quite similar to a SEM, but has some distinct differences. The electron beam passes through the sample (transmission), where it is detected. In a TEM, the electrons that pass through the sample are detected, instead of the backscattered and secondary electrons which are detected in a SEM.

While passing through the sample, the electron beam causes X-rays to eject from the sample, which can be detected as well. Because the energy of the X-rays is characteristic to the atom of origin, elemental analysis of your sample is possible with a coupled EDX.²⁷

4.6.4 Temperature Programmed Reduction, Oxidation and Desorption

Temperature Programmed Reduction (TPR), Oxidation (TPO) and Desorption (TPD) are three catalyst characterization techniques, based on the sample principle.

With TPR, the chemical reaction between the catalyst and the reduction gas (H_2) is monitored while the temperature is increased linearly in time. A peak in the TPR data indicates the uptake of H_2 and gives information at which temperature the catalyst is reduced. TPO works the same, but with O_2 to check at which temperature the catalyst is oxidized.¹⁷

For TPD, an inert gas is flowed over the catalyst after which a reaction gas (NH_3) is adsorbed on the catalyst surface. The temperature is increased linearly in time and the desorption of the reaction gas is monitored. The resulting TPD data give information about the acid sites of the catalyst.²⁸

5. Research objectives

The goal of this project is to gain more insights in the selective oxidation reaction of ethylene to ethylene oxide on α -alumina supported silver catalysts. The focus lies on the effects of alkali promotion on the silver catalyst for this reaction. The main research question will therefore be:

What are the effects of alkali promoters on α -alumina supported silver catalysts for the epoxidation of ethylene?

To answer the research question more elaborately and easily, several parameters shall be varied. The research question will therefore be split up in the sub-questions:

- 1. Is there any difference in the catalytic performance of an alkali promoted catalyst when using different amounts of chlorine in the gas feed of the reaction?*
- 2. What is the promotional effect on the catalytic performance of the catalyst when using different alkali promoters?*
- 3. Will there be any difference in the catalytic performance of the catalyst when using different weight loadings of an alkali promoter?*
- 4. Is there any difference in the catalytic performance of an alkali promoted catalyst when using different precursors of the alkali promoter in the synthesis?*

The project consists of the synthesis of the catalysts, characterization of the catalysts, testing the catalysts and interpreting the resulting data.

To answer these questions,

First of all, one synthesized cesium catalyst with a 0.08 mol% cesium weight loading will be tested for the selective oxidation of ethylene. The amount of ethylene and oxygen will be kept constant and the amount of ethyl chloride will be varied. The catalyst will be tested without EC, with 0.9 ppm EC and with 1.8 ppm EC.

Then, several catalysts will be synthesized with the same alkali weight loading of 0.08 mol%, but each with a different alkali promoter. One catalyst will be kept unpromoted. The alkali promoters that will be used are sodium, potassium, rubidium and cesium and will be tested for the epoxidation of ethylene where the reaction feed will be kept constant.

After that, a cesium catalyst with a 0.04 mol% weight loading will be synthesized and tested with the same reaction feed as before. The catalytic data will be compared to the unpromoted catalyst and the 0.08 mol% cesium catalyst to see if there is any difference in the performance when changing the weight loading.

Finally, a 0.08 mol% cesium catalyst will be synthesized again, but this time with cesium carbonate (Cs_2CO_3) as the cesium precursor instead of cesium hydroxide monohydrate ($\text{CsOH} \cdot \text{H}_2\text{O}$), which is used for the other catalysts. The 0.08 mol% cesium catalysts with the different precursors will be compared to see if there are any differences in the catalytic performance.

6. Experimental methods

In this chapter, it will be described how the project is conducted in order to reach the research objectives.

6.1 Catalyst preparation

Silver oxalate was prepared by mixing an aqueous solution of silver nitrate ($\geq 99.0\%$, Sigma-Aldrich) with an aqueous solution of oxalic acid ($\geq 99.0\%$, Sigma-Aldrich) in a 2:1 mol ratio. To obtain the silver oxalate, the mixture was centrifuged, after which it was washed three times with milli-Q water dried overnight in static air at $60\text{ }^\circ\text{C}$.

For the catalysts without alkali promoters, a silver solution is made by dissolving the silver oxalate precursor ($\text{Ag}_2\text{C}_2\text{O}_4$) in an ethylenediamine (EDA) ($99+\%$, Acros Organics) and milli-Q water mixture in a $\text{Ag}_2\text{C}_2\text{O}_4/\text{EDA}/\text{MQ}$ mol ratio of 1:4:16.

The same silver solution is prepared for the alkali promoted catalysts, but the milli-Q water is replaced by the alkali promoter solutions. All silver solutions are prepared in vials wrapped in aluminum foil to prevent the decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ by light. The target weight loading for silver on the catalyst was 15wt% for all catalysts. The quantities of the chemicals used in the preparation of all the catalysts are shown in Table 1 (Supporting Information).

The alumina used is α -alumina with a $8\text{ m}^2\text{ g}^{-1}$ surface area and a 0.45 mL g^{-1} pore volume (BASF, Al-4196E), which was sieved to a fraction of $<212\text{ }\mu\text{m}$. For a typical catalyst synthesis, 1.5 g alumina was weighed on an analytical balance. The alumina was dried under vacuum for 2 hours at $200\text{ }^\circ\text{C}$, while stirred on a magnetic stirrer (IKA RCT classic) at ca. 110 RPM. The exact heating temperatures and rpm are given in Table 2 (Supporting Information).

All catalysts were prepared via incipient wetness impregnation. The silver and the alkali promoter salts were added simultaneously (co-impregnation).

The alkali promoter solutions are prepared by making a stock solution with the alkali precursors dissolved in milli-Q water (MQ). The stock solutions are diluted several times to obtain the right alkali solutions for the targeted weight loadings. Table 3 (SI) shows the quantities used for the first stock solution and Table 4 (SI) shows the dilutions of these stock solutions. One catalyst was prepared with cesium carbonate as the precursor, of which no stock solution was made.

The precursors for cesium were $\text{CsOH} \cdot \text{H}_2\text{O}$ and Cs_2CO_3 for potassium KOH (99.98% metals basis, 85% min, ABCR), for sodium NaOH (97% , Sigma-Aldrich) and for rubidium Rb_2CO_3 .

The alumina is impregnated with the silver solution by dropwise adding the solution to the support material, while being slowly stirred on a magnetic stirrer.

The impregnated alumina is removed from the vacuum and dried overnight in static air at $60\text{ }^\circ\text{C}$. After 5, 10 and 30 minutes of drying in the oven, the alumina was stirred manually to ensure a homogeneous distribution of the silver solution in the alumina.

The dried material was calcined in $25\% \text{ O}_2$ in N_2 for two hours at $215\text{ }^\circ\text{C}$ ($5\text{ }^\circ\text{C}/\text{min}$) with a GHSV of 7000. After calcination, the synthesized catalysts could be obtained.

6.2 Characterization

Crystal phase analysis was performed with X-Ray Diffraction (XRD) on a Bruker D2 Phaser with a Co K α source ($\lambda = 0.1789$ nm) in an angle range from 35° to 85° in 2θ . The step increment was 0.05° and the step time was 0.2 s step $^{-1}$.

Temperature Programmed Reduction (TPR) analysis was performed on an AutoChem II 2920 (Micromeritics). An U-shaped quartz reactor was loaded with 50 mg catalyst (90-150 μm) in between two layers of quartz wool. Prior to each measurement, the catalyst was dried in argon at 120 °C for 15 minutes and subsequently cooled to room temperature. During the measurement, the samples were heated from 30 °C to 600 °C in 5% H $_2$ in argon (25 mL min $^{-1}$ STP), with a 5 °C min $^{-1}$ heating ramp. The signal was monitored by a thermal conductivity detector (TCD).

Temperature Programmed Oxidation (TPO) analysis was performed with the same equipment and settings, except for the gasses used. The drying step was carried out in He and the measurement was performed in 5% O $_2$ in helium.

Temperature Programmed Desorption (TPD) was performed on an Autochem II 2920 (Micromeritics). An U-shaped reactor was loaded with approximately 80-100 mg of catalyst in between two layers of quartz wool. Prior to the measurement, the samples were dried in air at 400 °C for 30 minutes (50 mL min $^{-1}$ STP) and then cooled to 100 °C. For the measurements, the samples were heated from 100 °C to 700 °C (5 °C min $^{-1}$ ramp) in a 10% NH $_3$ in helium (25 mL min $^{-1}$ STP). The signal was monitored by a TCD.

To determine the weight loadings of silver and the alkali promoters, Inductively Coupled Plasma (ICP) spectroscopy was performed by Mikroanalytisches Laboratorium Kolbe in Oberhausen, Germany.

For the silver particle size analysis of the catalysts, Scanning Electron Microscopy (SEM) was used before and after the catalytic tests. A FEI Helios G3 UC microscope was used at 5-10 kV in immersion mode. Catalyst powder was deposited on stubs with sticky carbon tape. The prepared samples were sputter coated with a 7.5 nm PtPd layer by a Cressington 208HR Sputter Coater.

Using ImageJ software, the diameter of the silver particles was measured. For each sample, at least 200 different particles were measured. The surface averaged particle sizes ($d_{p,s}$) and standard deviations ($\sigma_{p,s}$) were calculated with equation 1:

$$d_{p,s} \pm \sigma_{p,s} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2} \pm \sqrt{\frac{1}{n} \times \sum_{i=1}^n (d_{p,s} - d_i)^2} \quad (1)$$

In this equation, n is the number of counted silver particles, i is the number of the particle and d_i is the measured particle diameter of particle i .

TEM-EDX was used to obtain information about promoter location. A FEI Talos F200X was used, operated at 200 kV for both Bright Field TEM and HAADF-STEM. EDX was performed with a Super-XTM EDX detector, imaging in STEM mode with spot size 6. To prepare the TEM grid, catalyst powder was placed on a watch glass. Isopropanol was added and the mixture was dispersed with a Pasteur pipette. After dispersion, 2-3 drops of the mixture were added with a Pasteur pipette to a copper TEM grid. The TEM grid was left to dry in air to evaporate the isopropanol.

6.3 Catalytic testing

The silver catalysts were sieved to a 90-150 μm fraction. A quartz plug-flow reactor with an internal diameter of 4 mm was loaded with 100 mg catalyst and 500 mg silicon carbide (SiC) (Alfa Aesar, >98%, 212–245 μm) in between two layers of quartz wool. The SiC was washed with HNO_3 (65%, AnalaR NORMAPUR analytical reagent; 10 mL $\text{g}_{\text{SiC}}^{-1}$). Afterwards, the SiC was washed three times with 500 mL milli-Q water and dried at room temperature overnight. The dried SiC was calcined at 800 °C. The reaction feed consisted of 7.5% ethylene and 2.1% O_2 in He gas with 0-2 ppm amounts of ethylene chloride (EC). The reaction temperature was 215 °C.

For the isomerization experiments, 200 mg promoted support was loaded in the same quartz plug-flow reactor. Ethylene oxide was flowed over the catalysts to see how much would be converted into AA. The gas feed was 7.5% EO in He gas.

The reaction products were analyzed every 15 minutes with an Interscience Compact GC 4.0, with two separate channels (Porabond Q column and Molsieve 5A column).

7. Results and discussion

In this chapter the results of the synthesis, characterization and catalytic evaluation of the catalysts are explained and discussed.

7.1 Silver and alkali deposition

ICP measurements were performed to determine the weight loadings of silver and the alkali metals. The theoretical and measured silver and alkali promoter weight loadings of the fresh catalysts are shown in Table 5. Almost all the samples show that the targeted silver weight loading is obtained. Only the sodium catalyst (0.08mol% Na-Ag/Al₂O₃) shows a silver weight loading different from what was expected. This might be caused by silver not being able to dissolve completely in the EDA/MQ mixture, leading to the alumina not being impregnated with the right amount of silver. Another possible explanation might be that it is caused by a human error during the impregnation. The targeted alkali promoter weight loadings were obtained for most of the catalysts. The weight loadings are relative to the weight of the whole catalyst.

Table 5

Overview of samples measured with ICP and their corresponding silver and alkali promoter weight loading. Samples are labeled as [mol% promoter][alkali]-(Ag)/Al₂O₃

Sample	Theoretical Ag loading (wt%)	Measured Ag loading (wt%)	Theoretical alkali loading (ppm)	Measured alkali loading (ppm)
0.08 Na-Al ₂ O ₃	0	<0.01	1000	859
0.08 K-Al ₂ O ₃	0	<0.01	1000	896
0.08 Cs-Al ₂ O ₃	0	<0.01	1000	479
0.08 Na-Ag/Al ₂ O ₃	15	9.75	1000	699
0.08 K-Ag/Al ₂ O ₃	15	14.12	1000	877
0.08 Rb-Ag/Al ₂ O ₃	15	14.41	1000	901
0.04 Cs-Ag/Al ₂ O ₃	15	13.45	500	411
0.06 Cs-Ag/Al ₂ O ₃	15	13.51	750	634
0.08 Cs-Ag/Al ₂ O ₃	15	13.64	1000	986
0.08 Cs-Ag/Al ₂ O ₃ CO ₃	15	13.58	1000	679

7.2 Silver particle analysis

Once the catalysts were prepared, SEM was used to determine the silver particle size for each catalyst before and after catalysis. Figure 3 shows the SEM images of Ag/Al₂O₃, 0.08Na-Ag/Al₂O₃, 0.08K-Ag/Al₂O₃, 0.08Cs-Ag/Al₂O₃, 0.08Rb-Ag/Al₂O₃ and 0.08Cs-Ag/Al₂O₃_CO₃ with the corresponding histograms of the silver particles below. The grey and dark grey visible in the images is the alumina support and the white and light grey spots are the silver particles. The surface averaged particles sizes are listed in Table 6. The aim was to have catalysts that would all have the same silver particle size between 50 and 70 nm.

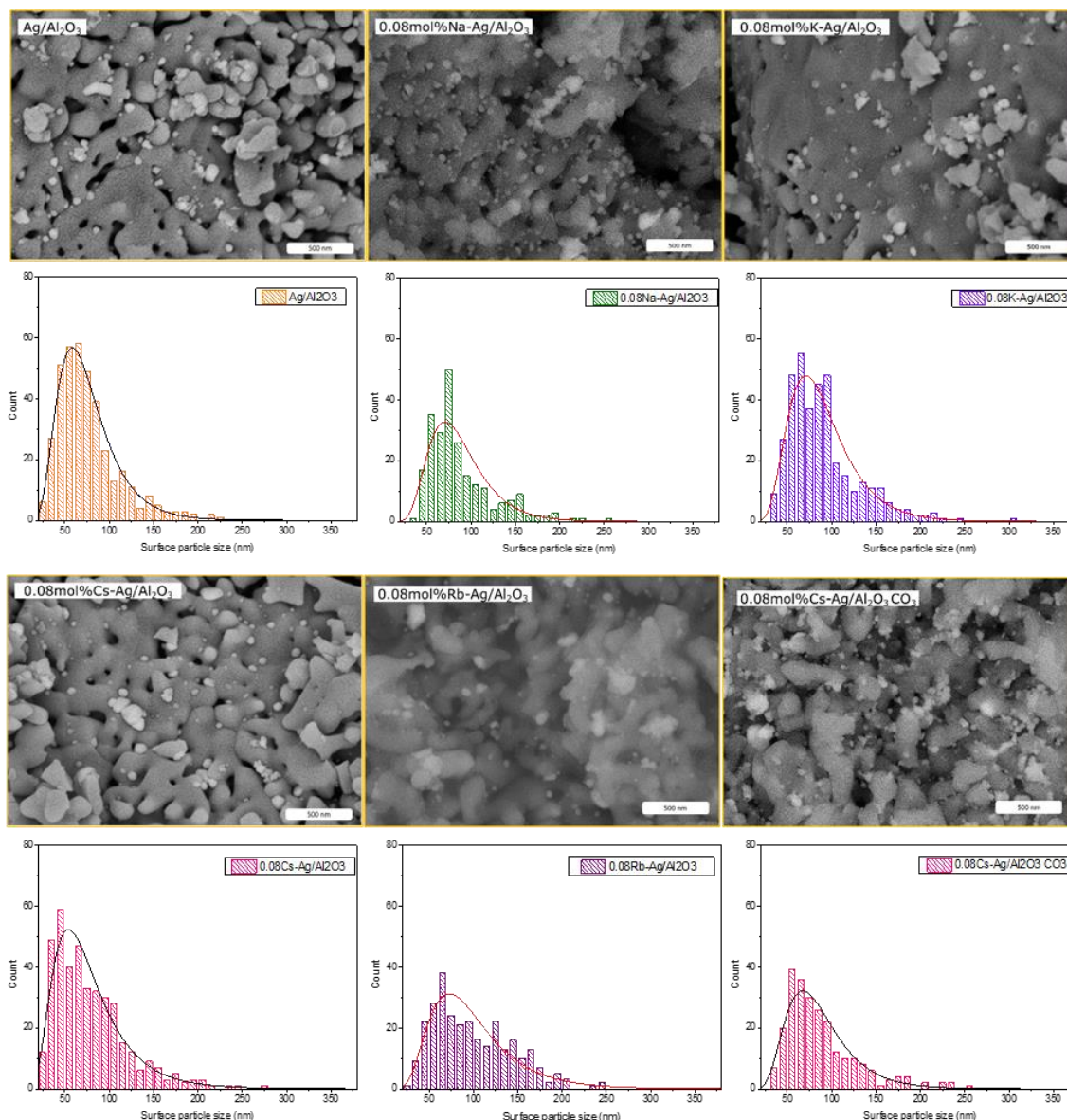


Figure 3. SEM images of the 0.08mol% promoted catalysts and of the unpromoted catalyst. Below each SEM image is the corresponding surface particle size histogram.

Table 6

Overview of the promoted and unpromoted silver catalysts. The surface average particle size with the standard deviation before and after catalysis are listed, together with the amount of ethyl chloride added to the reaction gas.

Catalyst	Surface average particle size of fresh catalysts (nm)	Ethyl chloride added during the reaction (ppm)	Surface average particle size of spent catalysts (nm)
Ag/Al ₂ O ₃	112 ± 50	1.8	135 ± 66
0.08mol% Na-Ag/Al ₂ O ₃	124 ± 83	1.8	142 ± 85
0.08mol% K-Ag/Al ₂ O ₃	130 ± 56	1.8	-
0.08mol% Rb-Ag/Al ₂ O ₃	138 ± 78	1.8	-
0.04mol% Cs-Ag/Al ₂ O ₃	104 ± 44	1.8	138 ± 67
0.08mol% Cs-Ag/Al ₂ O ₃	125 ± 62	0	145 ± 100
0.08mol% Cs-Ag/Al ₂ O ₃	125 ± 62	0.9	176 ± 89
0.08mol% Cs-Ag/Al ₂ O ₃	125 ± 62	1.8	126 ± 47
0.08mol% Cs-Ag/Al ₂ O ₃ CO ₃	130 ± 87	1.8	167 ± 125

The particle sizes of the fresh catalysts range from 104 to 130 nm. The SEM images and their corresponding particle size histograms of the unpromoted and the 0.08mol% promoted catalysts are shown below in Figure 2. The particles might be bigger than the ideal particle size, but they are fairly similar in size to one another. This is desired, because the particle size needs to be similar in order to compare the catalytic performance of the different catalysts and to be able to ascribe differences to the promoters and not to different particle sizes. After catalysis, most of the catalysts show particle growth. Only two samples show a bigger increase in particle size than the rest of the catalysts. The 0.08mol% Cs-Ag/Al₂O₃ 0.9EC has a growth of 50 nm and the 0.08mol% Cs-Ag/Al₂O₃ a growth of 37 nm. There were no images taken from the potassium and rubidium catalyst after the catalysis, so no particle size could be determined.

In Figure 4, the particle size of the spent catalyst is plotted against the particle size of the fresh catalyst. It can be seen that the 0.08 mol% Cs-Ag/Al₂O₃ 0.9EC and 0.08 mol% Cs-Ag/Al₂O₃ CO₃ catalysts have the biggest particle growth.

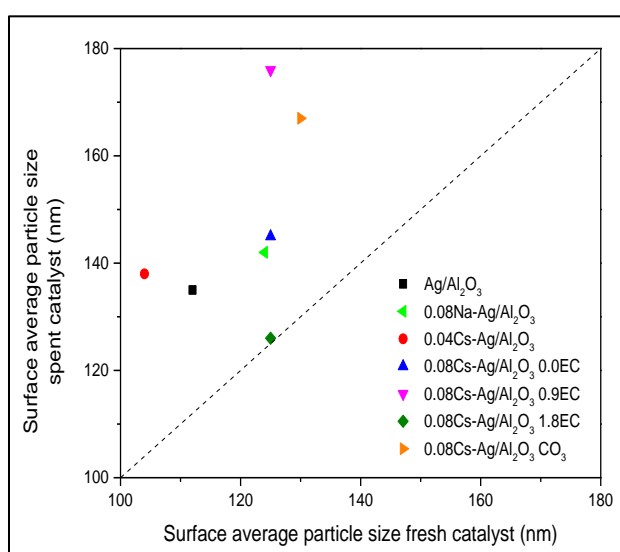


Figure 4. The surface average particle sizes of several spent catalysts plotted against the particle sizes of the fresh catalysts.

Since these two catalysts both have the highest weight loadings of cesium, it might the cesium is responsible for the silver particle growth.

7.3 Ethylene epoxidation

The synthesized catalysts were tested for the selective oxidation of ethylene to ethylene oxide. After testing the catalysts, the selectivity and conversion were calculated with equations 2 and 3 (SI):

7.3.1 Effect of ethyl chloride concentration

In order to determine the effect of ethyl chloride concentration on catalytic performance of the catalysts, the 0.08 mol% Cs-Ag/Al₂O₃ catalyst was tested with different amounts of chlorine added to the reaction feed. The reaction feed consisted of 7.5 vol% ethylene and 2.1 vol% O₂ in helium, where the amount of ethyl chloride was changed from 0 to 0.9 and 1.8 ppm. The conversion and selectivity data were plotted against the time and are shown in Figure 5. The reaction without the chlorine promotion shows with 5.5% the highest conversion. An increase and decrease in conversion are visible when EC is added to the reaction feed: at three hours when 1.8 ppm EC is added and at six hours when 0.9 ppm EC is added. Subsequently, the conversion decreases and slowly stabilizes at 3% (1.8 ppm EC) and 4% (0.9 ppm EC), although the conversion does not seem to be completely stabilized yet.

Not promoting the catalyst with chlorine during the reaction leaves the selectivity at just 20%. The selectivity increases with the addition of 0.9 ppm ethyl chloride, but adding 1.8 ppm EC seems to decrease the selectivity slightly. The addition of 0.9 ppm EC shows a selectivity of 55% and adding 1.8 ppm EC shows a selectivity 50%.

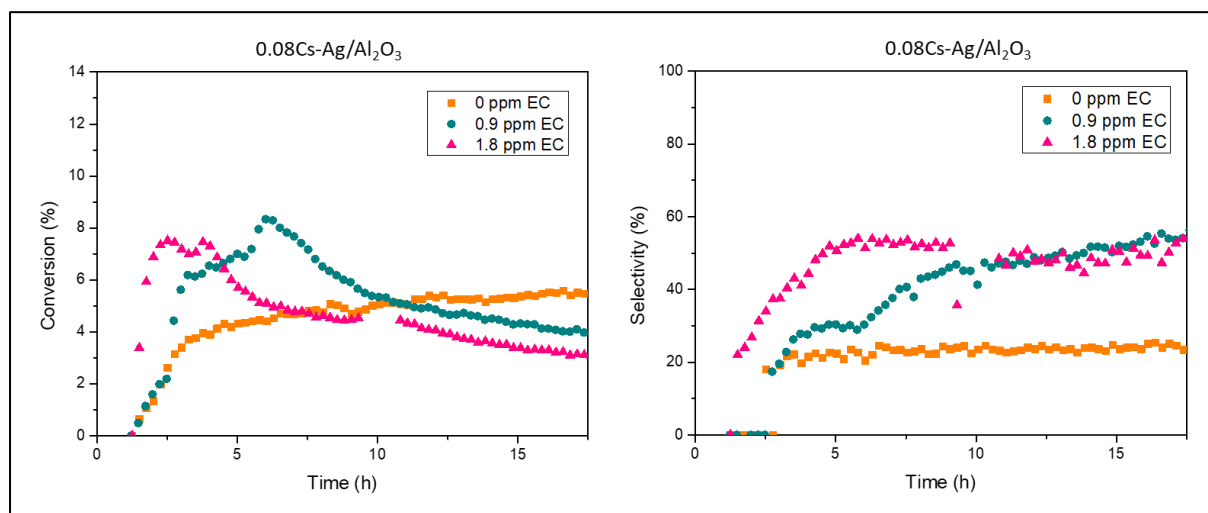


Figure 5. The conversion (left) and selectivity (right) plots of the 0.08Cs-Ag/Al₂O₃ catalyst for the selective oxidation of ethylene with different amounts of EC added to the reaction feed.

It can be seen in Figure 5 that the addition of EC leads to an increase in selectivity at the cost of activity, which is in line with literature. When increasing the concentration of ethyl chloride, an increase in the selectivity is observed. This is due to chlorine blocking the vacant sites next to the adsorbed oxygen. That way, the ethylene has no place to interact with the silver surface and is forced to react via the Eley-Rideal mechanism, which favors EO formation. This explains the decrease in conversion as well. Chlorine blocking these vacant sites means there is less place for oxygen to adsorb, which is why the conversion decreases. Having more ethyl chloride added to the reaction feed leads to an increase in selectivity to ethylene oxide, while decreasing the conversion.

7.3.2 Using different alkali promoters

The conversion and the TOF of the 0.08mol% promoted catalysts and the unpromoted catalyst were plotted against the reaction time and are shown below in Figure 6. The activity data of all catalysts except the Rb-promoted catalyst show a big increase and decrease in the first five hours, which can be assigned to the addition of chlorine in the reaction gas feed. The more relevant data is found after ten hours, once the activity stabilized. The conversion is shown on the left, where all catalysts seem to

have the same activity. Looking at the apparent turnover frequency (TOF) on the right, it is visible that the sodium catalyst has a TOF that is $0.02 \text{ mol mol}^{-1} \text{ s}^{-1}$ higher than the rest of the catalysts.

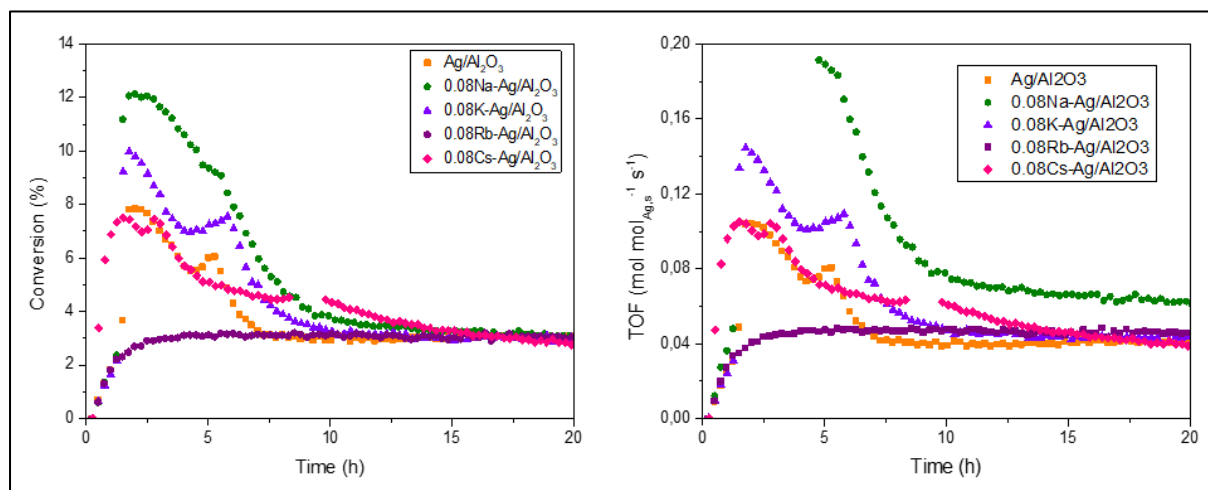


Figure 6. The activity data of the unpromoted and 0.08mol% promoted catalysts.

The Rb-promoted catalyst is the only catalysts that does not show an increase and decrease in conversion. This might suggest there is no chlorine present, although it is added during the reaction. A rubidium chloride species might be formed, causing the chlorine not being able to act as a promoter.

Figure 7 shows the selectivity data of the unpromoted catalyst and different promoted catalysts. The unpromoted catalyst and the Rb-promoted catalyst show with 70% the highest selectivity towards ethylene oxide. The Na-promoted catalyst has a slightly lower selectivity of 65%. The K-promoted catalyst shows a selectivity of 55% and the Cs-promoted catalyst shows the lowest selectivity of 50%.

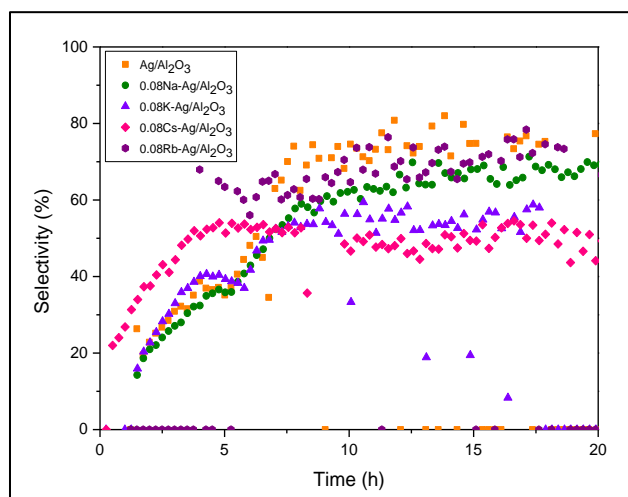


Figure 7. The selectivity plot of the unpromoted catalyst and the 0.08 mol% promoted catalysts.

Here, rubidium has a selectivity just as high as the unpromoted catalyst. The rest of the catalysts have a lower selectivity, where going down in the periodic table seems to decrease the selectivity.

7.3.3 Effect of cesium weight loading

To study the effects of different alkali weight loadings, catalysts were prepared with 0.04 and 0.08 mol% cesium. These catalysts, along with an unpromoted silver catalyst, were tested for the selective oxidation of ethylene to ethylene oxide. Figure 8 shows the conversion and selectivity plots, where the conversion and selectivity are plotted against the time. The increase and decrease in activity at three

hours can again be assigned to the addition of chlorine, after which the activity stabilizes. The 0.08 mol% cesium and the unpromoted catalyst show the same conversion of 3%, whereas the 0.04 mol% cesium catalyst shows a lower activity with a conversion of 1.5%.

The unpromoted catalyst shows the highest selectivity towards ethylene oxide. It shows a selectivity of 70%, while the 0.04Cs-Ag/Al₂O₃ catalyst shows a selectivity of 60% and the 0.08Cs-Ag/Al₂O₃ catalyst 50%.

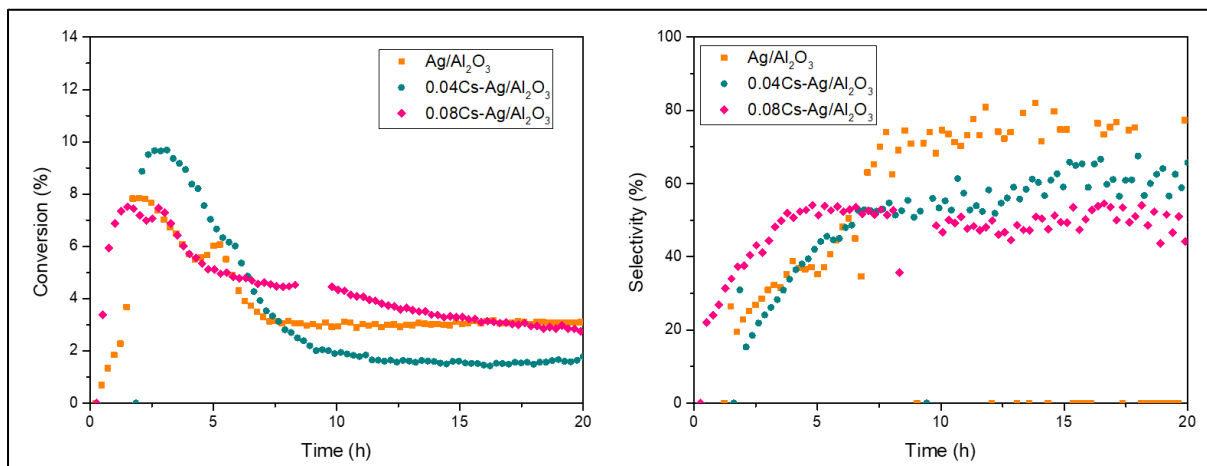


Figure 8. The conversion (left) and selectivity (right) plots of catalysts with different alkali weight loadings for the selective oxidation of ethylene.

Since the selectivity is dependent on the conversion, where the selectivity increases when decreasing the conversion, it might suggest that the 0.04 mol% cesium catalysts would have the highest selectivity towards EO. It has indeed a higher selectivity than the 0.08 mol% cesium catalyst, but the unpromoted catalysts shows the highest selectivity.

Figure 9 shows the selectivity plotted against the conversion. It can be seen that both the 0.04 mol% cesium and the 0.08 mol% cesium catalysts follow similar trends. This indicates that the increase in selectivity is caused by the decrease in conversion. The difference in selectivity can therefore not be assigned to the difference in the alkali weight loading.

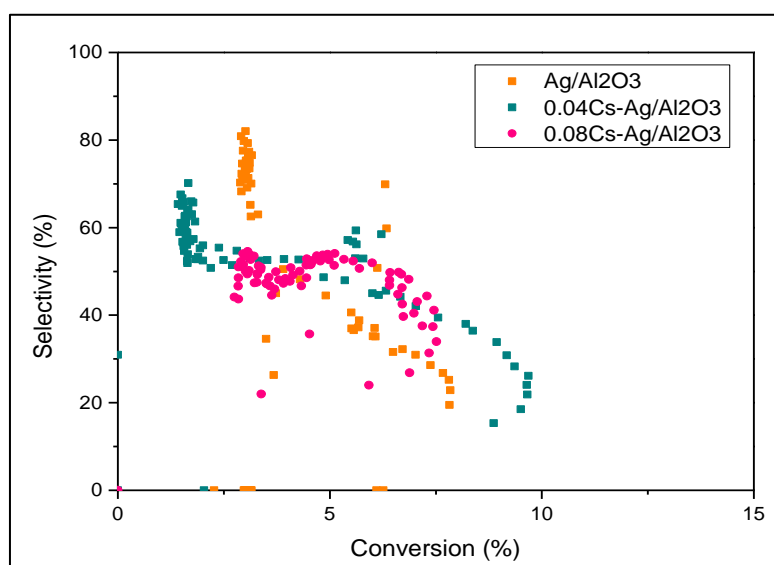


Figure 9. The selectivity plotted against the conversion of the Ag/Al₂O₃, 0.04Cs-Ag/Al₂O₃ and 0.08Cs-Ag/Al₂O₃ catalysts.

ICP showed that the 0.04 mol% cesium catalyst has a cesium weight loading of 411 ppm and the 0.08 mol% cesium catalyst has a weight loading of 986 ppm cesium. While one catalyst has double the

amount of cesium present than the other, they show the same selectivity versus conversion trends. This agrees with literature, where it is stated by Diao et al²⁹ and Lauritzen³⁰ that 350 ppm cesium is the optimal weight loading to gain the highest EO selectivity, while Ren¹⁰ calculated that approximately 800 ppm cesium would be the optimal weight loading for the highest EO selectivity.

The unpromoted catalyst however, shows a higher selectivity than both of the promoted catalysts, while having the same conversion as the 0.08 mol% cesium catalyst. This high selectivity is not caused by a decrease in the conversion. Promoting the catalyst with cesium lowers the selectivity, which contradicts with the generally accepted theory that cesium increases the selectivity towards EO.

To further investigate why the unpromoted catalyst shows the highest selectivity, TPO measurements were performed. Figure 10 shows the TPO data of the 0.08 mol% cesium catalyst and the unpromoted catalyst, where the TCD concentration is plotted against the temperature.

The Ag/Al₂O₃ catalyst shows a peak at 205 °C, meaning there is an oxygen uptake at this temperature. The peak shifts towards 225 °C when the catalyst is promoted with 0.08 mol% cesium. The cesium promoted catalyst gets oxidized at a higher temperature.

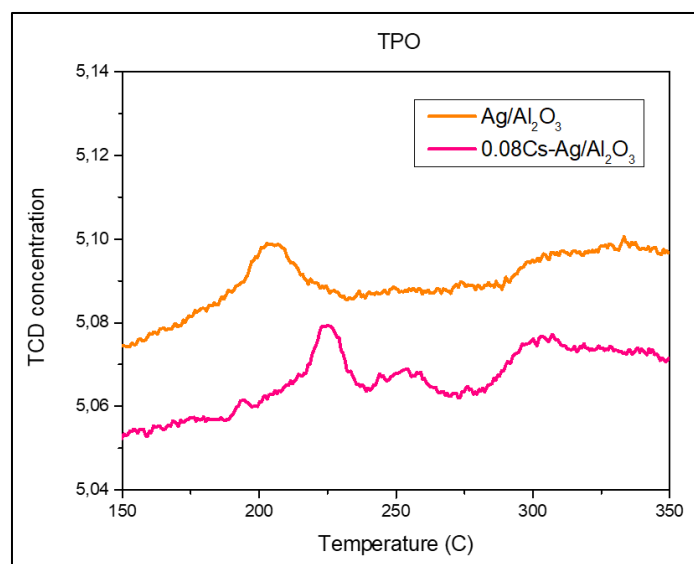


Figure 10. TPO graph of the unpromoted and 0.08 mol% cesium promoted catalysts.

The temperatures of calcination and of the epoxidation reaction are both 215 °C. At this temperature, the Ag/Al₂O₃ catalyst gets more oxidized than the 0.08 mol% Cs-Ag/Al₂O₃ catalyst. It might suggest that a silver oxide species is formed on the Ag/Al₂O₃ catalyst during these reactions, which can act as an active species for epoxidation. With the promotion of the catalyst with cesium, the oxidation might be blocked by the cesium promoters, thereby decreasing the formation of a silver oxide species and thus decreasing the selectivity.

The selectivity towards ethylene oxide seems to decrease with an increasing amount of cesium promoter added to the catalyst.

7.3.4 A different cesium precursor

To determine the effect of the precursor used on the catalytic performance, two Cs-promoted catalysts were tested for the epoxidation of ethylene. One made with the cesium hydroxide precursor and the other with the cesium carbonate as the precursor. The conversion and selectivity data are shown in Figure 11. The carbonate catalyst shows a conversion of 4%. This is 1% higher than the conversion of the hydroxide catalyst, which is 3%. The carbonate catalyst shows a higher selectivity as well. It has a EO selectivity of 65%, compared to a 50% EO selectivity of the hydroxide catalyst.

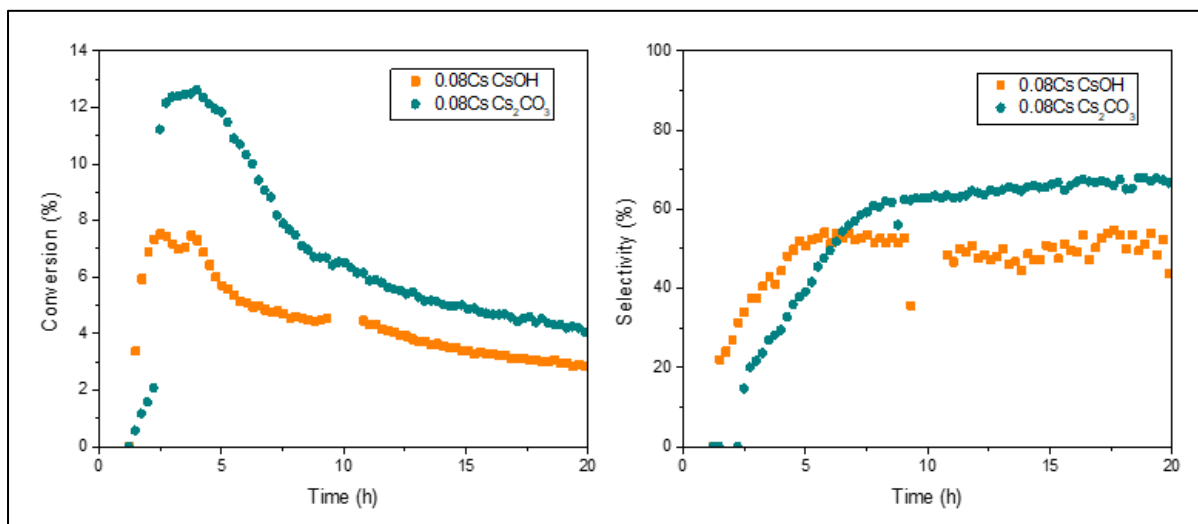


Figure 11. The conversion (left) and selectivity (right) plots of the 0.08Cs-Ag/Al₂O₃ catalysts for the selective oxidation of ethylene. In orange is the catalyst prepared with the hydroxide precursor and in green the catalyst prepared with the carbonate precursor.

The catalyst prepared with the carbonate precursor shows a better catalytic performance than the hydroxide precursor in both the conversion and the selectivity. A possible explanation can be that it is easier for the cesium to get into the pores of the support and get more evenly distributed when the carbonate precursor is used in the impregnation solution. Using the hydroxide precursor in the impregnation solution affects the pH and might disfavor a homogeneous distribution, leading to a lower conversion and selectivity.

The choice of precursor does affect the catalytic performance of the catalyst. The use of cesium carbonate as the precursor results in a higher conversion and selectivity compared to the hydroxide precursor.

8. Conclusions

The goal of this project was to investigate the effects of alkali promotion on silver catalysts for the epoxidation of ethylene. More precisely, the effect of ethyl chloride concentration during the reaction was investigated. The effect of different alkali promoters was studied, as well as the effect of different weight loadings of cesium. At last, the effect of a different cesium precursor was investigated.

This was carried out by synthesizing the catalysts via incipient wetness impregnation. The silver particle size of the catalysts was measured from SEM images and the weight loadings of the silver and the alkali metals were determined with ICP.

The catalysts were tested for the epoxidation of ethylene. Increasing the concentration of ethyl chloride led to an increase in selectivity, while a decrease in conversion was observed.

Preparing catalysts with different alkali metals showed that all the promoted catalysts had a lower selectivity compared to the unpromoted catalyst, except the rubidium promoted catalyst. The rubidium promoted catalyst had a similar selectivity as the unpromoted catalyst.

Promoting the catalyst with 0.04 and 0.08 mol% cesium showed a decrease in selectivity, where the 0.08 mol% cesium catalysts showed the largest decrease.

The cesium catalyst prepared with a cesium carbonate showed a higher selectivity and higher conversion than the one prepared with cesium hydroxide.

9. Outlook

This study gives us some more information about the mechanism of ethylene epoxidation, but this study can be continued and improved in the future. A lot of catalysts have been made, but only a selected handful have been tested. Testing the rest of the catalysts would provide more information about the catalytic performance when using different silver and alkali metal weight loadings.

This would also mean that more catalysts need to be prepared, since at the moment for Rb promotion only the 0.08mol% Rb catalyst is synthesized. The 0.02mol%, 0.04mol% and 0.06mol% Rb samples could be made to better compare and understand the catalysts.

It would also mean that more SEM images need to be taken in order to determine the particle size.

To complete the row of alkali metals, lithium promoted silver catalysts could be synthesized with different weight loadings as well. In addition, the TPO data could be completed by measuring the Rb catalyst and the TPD measurements of most of the samples should be repeated to properly compare the data and gain more insights into the isomerization mechanism.

At last, it might be great to perform XPS measurements to get a better understanding of the interaction between the silver and promoter particles.

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Supporting information

1. Tables

Table 1

Overview of the amount of chemicals used for the preparation of each catalyst. Target weight loading for silver is 15wt% for all samples. The mol% shown is the mol% of the corresponding alkali promoter. Column 5 shows the amount of stock of the stock given in column 4, which refers back to the stocks in table 2 or 3.

Sample	Al ₂ O ₃ (g)	EDA (g)	Stock (nr.)	Stock (g)	MQ (g)	Ag ₂ C ₂ O ₄ (g)
Ag/Al ₂ O ₃ 1	0.87722	-	#1	0.39583	-	0.20900
Ag/Al ₂ O ₃ 2	1.50278	-	#1	0.65334	-	0.31602
0.02mol% Na-Ag/Al ₂ O ₃	1.50710	0.29060	#11	0.35339	-	0.36725
0.04mol% Na-Ag/Al ₂ O ₃	1.50302	0.29500	#10	0.34209	-	0.38171
0.06mol% Na-Ag/Al ₂ O ₃	1.49873	0.28300	#9	0.34776	-	0.37150
0.08mol% Na-Ag/Al ₂ O ₃	1.50407	0.28250	#8	0.36133	-	0.37961
0.16mol% Na-Ag/Al ₂ O ₃	1.49999	0.29460	#2	0.35776	-	0.34128
1wt% Na-Ag/Al ₂ O ₃	1.50045	0.30640	#3	0.34950	-	0.36535
0.02mol% K-Ag/Al ₂ O ₃	1.49361	0.30	#14	0.35345	-	0.38690
0.04mol% K-Ag/Al ₂ O ₃	1.49584	0.29	#13	0.34312	-	0.37607
0.06mol% K-Ag/Al ₂ O ₃	1.49769	0.29	#12	0.36007	-	0.3690
0.08mol% K-Ag/Al ₂ O ₃	1.50390	0.29	#4	0.36038	-	0.36610
0.08mol% Rb-Ag/Al ₂ O ₃	1.49789	0.29	#15	0.36	-	0.38
0.04mol% Cs-Ag/Al ₂ O ₃	1.10032	0.22	#6	0.13377	0.13080	0.26441
0.06mol% Cs-Ag/Al ₂ O ₃	1.10342	0.21	#6	0.19125	0.06721	0.23300
0.08mol% Cs-Ag/Al ₂ O ₃ 1	1.49439	0.30	#6	0.36	-	0.36980
0.08mol% Cs-Ag/Al ₂ O ₃ 2	1.49808	0.29	#6	0.35	-	0.36573
0.08mol% Cs-Ag/Al ₂ O ₃ CO ₃	1.49880	0.29954	#17	0.35696	-	0.39286

Table 2

Overview of all the weights of alumina, at which speed the magnetic stirrer is spun and at which temperature the stirrer was set. One sample was dried on a different heater, where only the heating level is given.

Sample	Al ₂ O ₃ (g)	RPM	T stirrer (°C)	Heating level
1	0.87722	120	220	-
2	1.50278	-	-	4
3	1.50710	110	220	-
4	1.50302	110	220	-
5	1.49873	110	220	-
6	1.50407	120	220	-
7	1.49999	120	210	-
8	1.50045	120	210	-
9	1.49361	120	220	-
10	1.49584	120	220	-
11	1.49769	120	220	-
12	1.50390	120	220	-
13	1.49789	120	220	-
14	1.10032	110	220	-
15	1.10342	110	220	-
16	1.49439	110	220	-
17	1.49808	110	230	-
18	1.49880	120	220	-

Table 3

Overview of the quantities of MQ and the precursors in the stock solutions. The compounds behind the slash in the stock solutions column are the precursors used.

Stock (nr.)	Stock solutions	EDA (g)	MQ (g)	Precursor (g)
#1	MQ / EDA	4.47	5.52	-
#2	MQ / NaOH 1	-	34.95890	0.10745
#3	MQ / NaOH 2	-	35.01870	3.05383
#4	MQ / KOH	-	37.90691	0.08100
#5	MQ / Rb ₂ CO ₃	-	35.35270	0.30110
#6	MQ / CsOH · H ₂ O	-	35.38350	0.13090
#7	MQ / Cs ₂ CO ₃	-	35.33050	0.43700

Table 4

It shows the new stocks made from diluting the stocks in Table 2.

Stock (nr.)	Dilution	of Stock (nr.)	Stock (g)	MQ (g)
#8	2x	#2	3.03013	3.02016
#9	1.5x	#8	0.30985	0.09905
#10	2x	#8	1.00445	0.99297
#11	2x	#10	0.25084	0.25282
#12	1.5x	#4	0.30935	0.10710
#13	2x	#4	1.199	1.204
#14	2x	#13	0.36154	0.37064
#15	2x	#5	4.98926	5.00896
#16	2x	#6	4.99472	5.05333
#17	2x	#7	10.00695	9.99490

2. Calculations of selectivity, conversion and TOF

The selectivity, conversion and turnover frequency are calculated with the following equations:

$$\text{Selectivity} = \frac{EO}{0.5 \times CO_2 + EO + AA} \times 100\% \quad (2)$$

$$\text{Conversion} = 1 - \frac{\text{Ethylene}_{out}}{\text{Ethylene}_{t=0}} \times 100\% \quad (3)$$

The TOF could be calculated from the conversion values with equation 4:

$$\text{TOF} = \frac{\text{Ethylene converted (mol s}^{-1}\text{)}}{A_{g_{\text{surface atoms}}} \text{ (mol)}} \quad (4)$$

In this equation, *ethylene converted* is calculated with equations 5 and 6.

$$\text{Ethylene converted (mol s}^{-1}\text{)} = \text{Ethylene}_{in} \text{ (mol s}^{-1}\text{)} \times \frac{\text{Conversion (\%)}}{100} \quad (5)$$

$$\text{Ethylene}_{in} \text{ (mol s}^{-1}\text{)} = \frac{\frac{\text{Ethylene}_{in} \text{ (mL min}^{-1}\text{)}}{V_m \text{ (mL}^3 \text{ mol}^{-1}\text{)}}}{60} \quad (6)$$

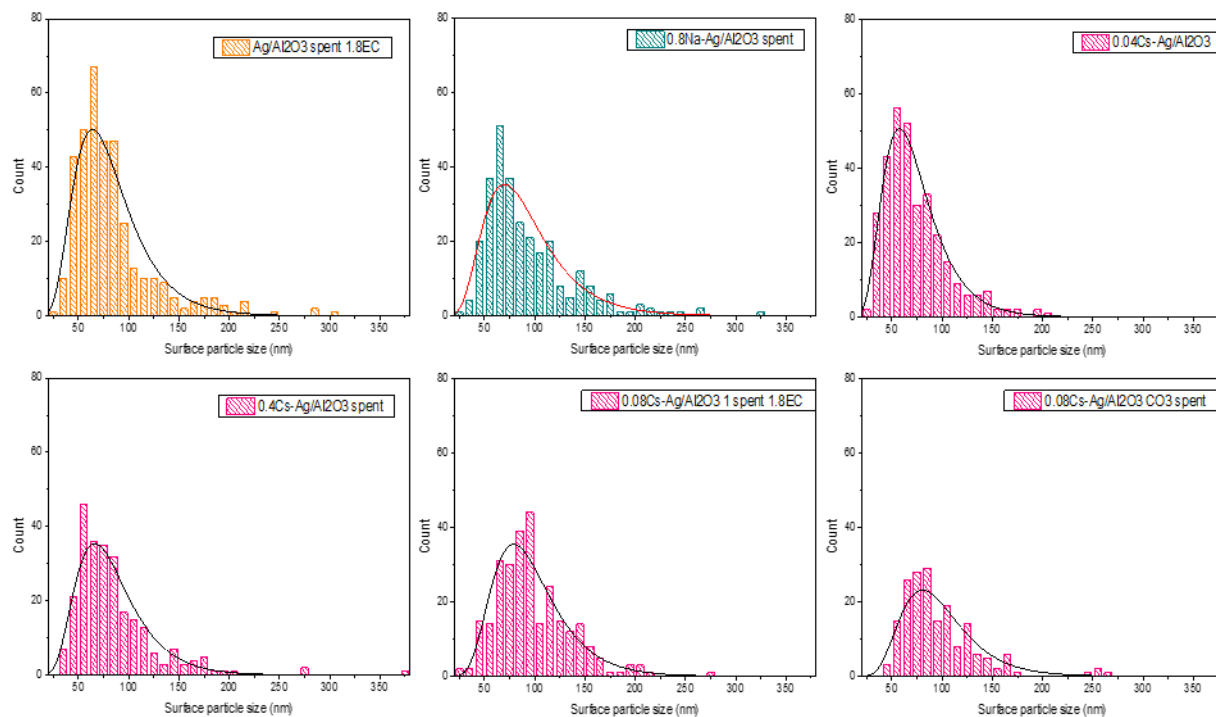
The $A_{g_{\text{surface atoms}}}$ from equation 4 is calculated with equations 7 and 8.

$$A_{g_{\text{surface atoms}}} \text{ (mol)} = \text{Dispersion} \times A_g \text{ (mol)} \quad (7)$$

$$\text{Dispersion} = \frac{\frac{\frac{4}{3}\pi \times (\text{radius Ag atom})^3}{\pi \times (\text{radius Ag atom})^2} \times 6}{\text{Diameter Ag}_s \text{ (nm)}} \quad (8)$$

3. Surface particle size histograms

Shown below are extra particle size histograms of spent catalysts.



4. XRD

XRD was performed to study the crystalline phase of the silver particles and to determine if the decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ to Ag was successful. The figure below shows the XRD diffractogram of the unpromoted catalyst and different cesium promoted catalysts. The fact that sharp peaks are visible means that the silver particles are metallic and that the silver oxalate has decomposed. If the peaks were not sharp, it could indicate the presence of silver oxide, since silver oxide is amorphous and would give rise to a broad hump in the XRD spectrum. The silver peaks are indicated with an asterisk and are positioned at 44.6° , 51.9° and 76.5° . The peaks correspond to the (111), (200) and (220) planes, respectively.

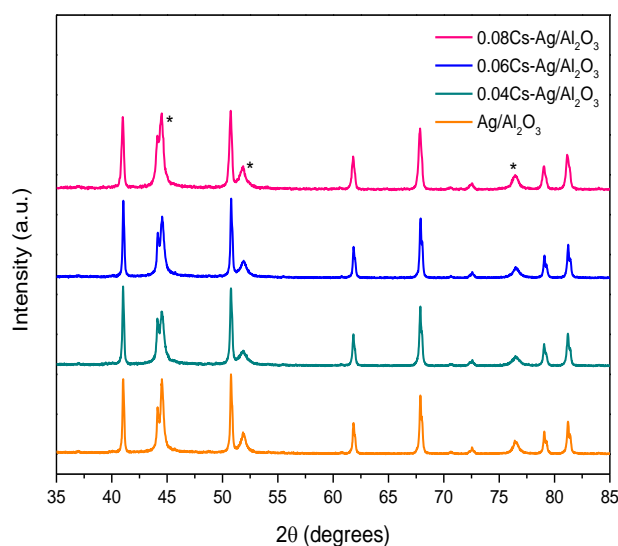


Figure 4. The XRD diffractogram of cesium promoted catalysts with different weight loadings and the unpromoted catalyst. The asterisks indicate the silver peaks at 44.6° , 51.9° and 76.5° . The other peaks can be assigned to α -alumina.

5. TEM images

When TEM images were taken for the first time, chlorine was visible on the silver particles of some of the samples via EDX characterization (Figure 1). This was undesired and unexpected, because the chlorine needs to be added to the gas feed and not on our catalyst during the synthesis. Chlorine can be added during the preparation, but since we want to keep our parameters constant, that is subject for another study.

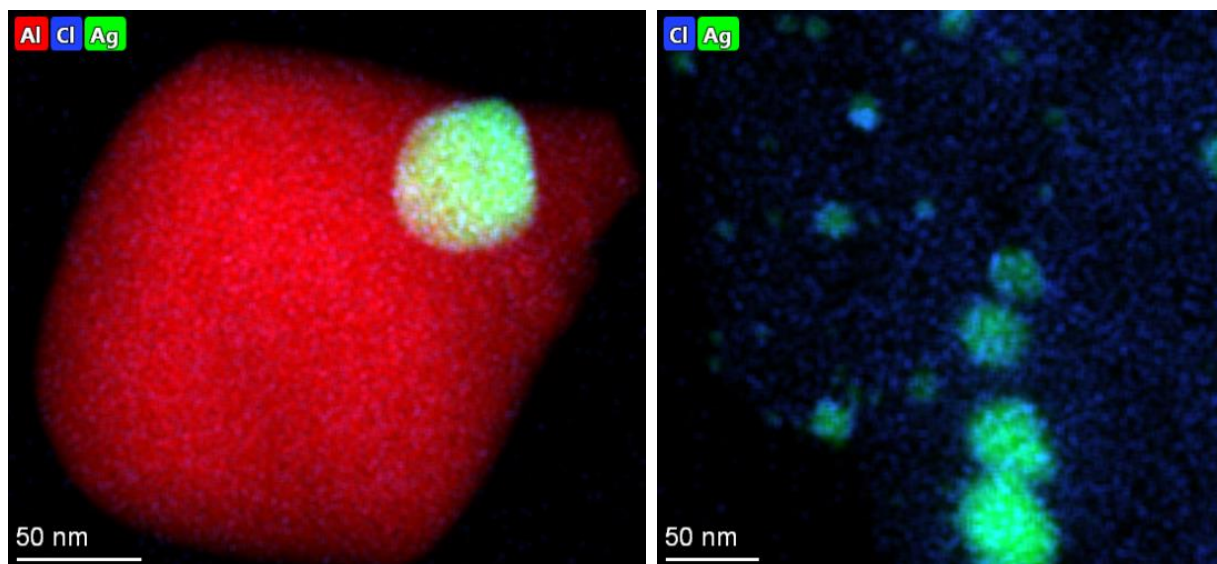


Figure 1. TEM images of samples where chlorine was believed to be present. The left image is from the 0.08Cs-Ag/Al₂O₃ catalyst and the right image from the 0.08K-Ag/Al₂O₃ catalyst. Red represents the aluminum, green the silver and blue the chlorine.

It was found that the KOH precursor is industrially synthesized by electrolysis of potassium chloride. If there were very little traces of KCl left behind, this might explain the chlorine on the catalyst. For this reason, one catalyst was synthesized again with a carbonate salt as precursor (0.08mol% Cs-Ag/Al₂O₃ CO₃). After this, it was concluded that it might not be chlorine after all, since the K_{β1} X-ray emission line of chlorine (2815.6 eV) overlaps with the L_{α1} and L_{α2} X-ray emission lines of silver (2984.31 eV and 2978.21 eV, respectively). To ensure that there was indeed no chlorine on the catalysts, the remaining samples yet to be measured with ICP were also tested for the presence of chlorine. One sample previously tested (0.08mol% Cs-Ag/Al₂O₃) was measured again, this time also for chlorine.

All the samples were free of chlorine, except one. The sample that was measured again had a chlorine weight loading of 409 ppm. This time, it had a significant lower silver and cesium weight loading as well, respectively 4.12wt% and 119 ppm. The lower silver and cesium weight loadings could be explained by not having the silver and cesium homogeneously dispersed on the alumina support. The submitted sample was just a part with less silver and cesium deposited on it. Incipient wetness impregnation is a deposition method known to be difficult to get a homogeneous particle distribution. Why there is chlorine present on the catalyst can be for several reasons. It might be that during the catalyst preparation there were some chlorine traces left on equipment used. Another reason could be that chlorine was already in the precursor used.