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# Investigation of the Yara 58-Y1 nitrous oxide decomposition catalyst

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## Preface

This master thesis is a continuation of a specialization project done last semester at the catalysis group at the department of chemical engineering at NTNU. The project is a collaboration between NTNU and the YARA technology center.

YARA is a chemical company with roots in the early Norwegian industrialization and is heavily involved in amongst other things, fertilizer production. As a premiere company in chemical industry, having good catalysts for its processes is vital and it actively develops catalysts itself. Among the catalysts developed at YARA is the 58-Y1 nitrous oxide abatement catalyst designed to clean nitrous oxide created in the production of nitric acid. The catalyst uses cobalt aluminate with a cerium oxide support. It has been observed that the grade and origin of the cerium oxide has a significant effect on the properties of the final catalysts, though it is unclear what exactly is responsible for this. The goal of this project was to investigate two grades of cerium oxide and their catalyst counterpart in order to build an understanding of their properties.

I would like to thank my supervisor Magnus Rønning for advice and input during the project. I would also like to thank David Waller at YARA and the YARA Technology Center in Porsgrunn for creating an interesting project to work on. Finally I would like to thank Harry Brun for the significant amounts of nitrogen consumed, Arne Fossum, which always had equipment for me, Karin W. Dragsten for general instrument support and Julian Tolchard for XRD support.

Investigation of the 58-Y1 was also done by Ørjan Berntsen at the Department of Physics using TEM Transmission Electron Microscopy (TEM), which allows very high magnification to be achieved. Results of his findings will be referenced in this report and I thank him for his cooperation during the project.

### Declaration of compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU) .

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## Abstract

The YARA 58-Y1 catalyst is a catalyst developed by YARA for the abatement of nitrous oxide created during nitric acid production. It uses cobalt aluminate ( $\text{Co}_2\text{AlO}_4$ ) as its active phase supported on cerium oxide. The active material itself makes up around 2% of the final catalyst. The catalyst is effective and gives a high conversion with little deactivation over time, though the cerium oxide grade used appear to have a major impact on final catalyst performance. There would appear to be little consistency in the properties giving a good catalyst, as different grades of high and low surface, acidic and basic cerium oxide can produce good or bad catalysts. To get a better understanding of the properties of the cerium oxide and how they relate to the final catalysts, two grades of cerium oxide, one high surface and one low surface, and the catalysts were investigated using BET nitrogen adsorption, X-ray diffraction (XRD) and scanning electron microscope (SEM). It was found that the catalysts had significantly lower surface area than the cerium oxide grades they were based on, but that the high surface cerium oxide catalyst had a higher surface area than the one based on low surface cerium oxide. Surface area was also lost for the high surface catalyst from unused to used sample, while for the low surface catalyst the difference was minor. Crystallite sizes followed surface area and the higher the crystallite size, the lower the surface area. Pore structure was virtually wiped out during catalyst creation. SEM indicated differences in structure, with the low surface catalyst more or less retaining structure through use, while the high surface catalyst became more crystalline. Due to there not being a significant difference in deactivation between the high and low surface catalysts, the performance differences probably stems from properties before or after production. The cobalt aluminate phases were similar between the high surface and low surface catalysts, indicating no major difference in cobalt particle size, as confirmed by TEM. The exact reason why the high surface catalyst performs better is still unknown, but could stem from a better contact surface with the cerium oxide, given that the cerium oxide/cobalt oxide interphase itself has significant catalytic activity. Other reasons might be structural in the catalyst pellets themselves.

## Sammendrag

YARA 58-Y1 er en katalysator utviklet av YARA for rensing av lattergass dannet i produksjon av salpetersyre. Katalysatoren bruker Koboltaluminat ( $\text{Co}_2\text{AlO}_4$ ) som den aktive fasen, støttet av ceriumoksid. Det aktive materiale utgjør ca. 2% av den endelige katalysatoren. Katalysatoren er effektiv og gir høy omdanning av lattergass uten å svekkes stort over tid. Det er slik at graden av ceriumoksid som brukes har en stor effekt på den endelige ytelsen til katalysatoren. Det er liten konsistens hvilke egenskaper som gir en god katalysator, om det er overflate, surhet mm. For å få en bedre forståelse av hva som avgjør hvilke egenskaper det er ved ceriumoksid som påvirker katalysatoren, er det undersøkt to grader av ceriumoksid, en med høy overflate og en med lav, og brukte og ubrukte katalysatorene basert på dem ved hjelp av nitrogenadsorpsjon (BET), røntgendiffraksjon (XRD) og scanning electron microscope (SEM). Det ble funnet at katalysatorene hadde betydelig lavere overflate enn ceriumoksidene de var basert på og at katalysatoren basert på høy overflate ceriumoksid hadde høyere overflate enn den basert på ceriumoksid med lav overflate. Katalysator basert på ceriumoksid med høy overflate mistet overflate etter bruk, mens den basert på lav overflate ikke gjorde dette i noen stor grad. Krystallittstørrelser fulgte overflaten og økte når ceriumoksid ble omgjort til katalysator. Porestrukturen ble også mer eller mindre fjernet i omdanningen til katalysator. SEM indikerte ulikhet i struktur, hvor katalysatoren med lav overflate beholdt sin struktur, mens den med høy overflate ble mer krystallinsk. Gitt at det ikke er noen stor forskjell i deaktivering mellom katalysatorene, indikerer dette at egenskaper som eksisterte før eller under katalysatorproduksjon er viktige for den endelige ytelsen. Koboltaluminatfasen var mer eller mindre lik for begge katalysatorene, som indikerer at det ikke var noen stor forskjell nå det gjaldt koboltpartikler, som også sett ved TEM. Den eksakte grunnen til ytelsesforskjellen er vanskelig å vite, men kan komme fra en bedre kontaktflate mellom koboltaluminatpartikler og støttematerialet, da det er slik at sjiktet mellom fasene har potensial for betydelig katalytisk aktivitet. Forskjellen kan også stamme fra strukturen i katalysatorpelletene.

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# 1. Introduction

While the start of the industrial revolution was a happy-go-lucky time where mercury was a thing one would dump in rivers and the main way to get rid of polluting gas was to build very high chimneys, such is no longer the case, at least in the western world. The standards for emissions grow ever higher and attempts are made to reduce emissions as cheaply and effectively as possible. Nitrous oxide is a powerful climate gas with a lifetime in the atmosphere of over a hundred years and is over three hundred times more effective at absorbing heat than carbon dioxide over its lifetime[1]. The abatement of nitrous oxide emission is therefore an interesting field and YARA has developed a catalyst, the 58-Y1 for use in abatement in connection with nitric acid production. The catalyst is commercial, effective and long lasting. It is based on a cerium oxide support, with cobalt aluminate as its active material. It has been discovered that different grades of cerium oxide have dramatic effects on the end catalysts, but it is unknown exactly what properties are important. Discovering the exact properties that makes the cerium oxide into a good catalyst has important implications, as allows greater flexibility to choose without risk of a poor end product. Being able to use a cheaper alternative may lead to both more profitable business, but also lower prices, allowing for abatement in more processes and places. The net gain for the environment is most desirable.

## 2. Theory

A catalyst is a material which participates in a reaction, but is not consumed in it. The purpose of the catalyst is to speed up the reaction by making the transition easier by lowering the energy needed to activate the reaction. It does not affect the final energy cost of the reaction itself and will not magically make an endotherm reaction into an exothermic reaction.

A catalyst often consists of both an active catalyst such as platinum, and a support, such as cerium oxide. The catalyst itself is the active part, while the support provides a stable platform. Making a catalyst of only active material is often undesirable, as the active material such as cobalt or platinum is often expensive, and in the case of cobalt it is carcinogenic and has other less desirable health effects[2]. Only the material on the surface is active in the reaction and for large particles a significant amount will be locked inside. Attempting to increase surface area through pores and smaller particles risks the structural stability of the catalyst both with respect to thermal and mechanical forces. A support is therefore desirable to provide a structure for attachment of smaller catalyst particles to maximize the amount of catalyst active in the reaction, aka the dispersion.

The YARA 58-Y1 catalyst is primarily used as a catalyst for decomposition of nitrous oxide created during the production of nitric acid. Nitrous oxide is dealt with by reducing it to base elements. This can be done using a catalyst, but will also happen by itself given enough temperature.

### 2.1 The nitric acid production process.

Nitric acid is produced through contacting  $\text{NO}_2$  with water. The  $\text{NO}_2$  is produced by combusting ammonia with air using a platinum/rhodium gauze to create  $\text{NO}$ . The combustion itself has three possible reactions[3].



Two of these reactions do not produce  $\text{NO}$  and are therefore undesirable. They are avoided by running the combustion at a high temperature and at a low residence time. The ammonia combustion takes place at a temperature of around  $850^\circ\text{C}$ [4]. Once the main combustion is done  $\text{NO}$  is oxidized to  $\text{NO}_2$  non-catalytically and the resulting  $\text{NO}_2$  is contacted with water to produce the nitric acid.



The creation of  $N_2O$  happens not only in the combustion itself, as seen above, but also in reaction with the produced  $NO$ , as seen below.



A flow sheet of the nitric acid production is seen below in Figure 1[5].

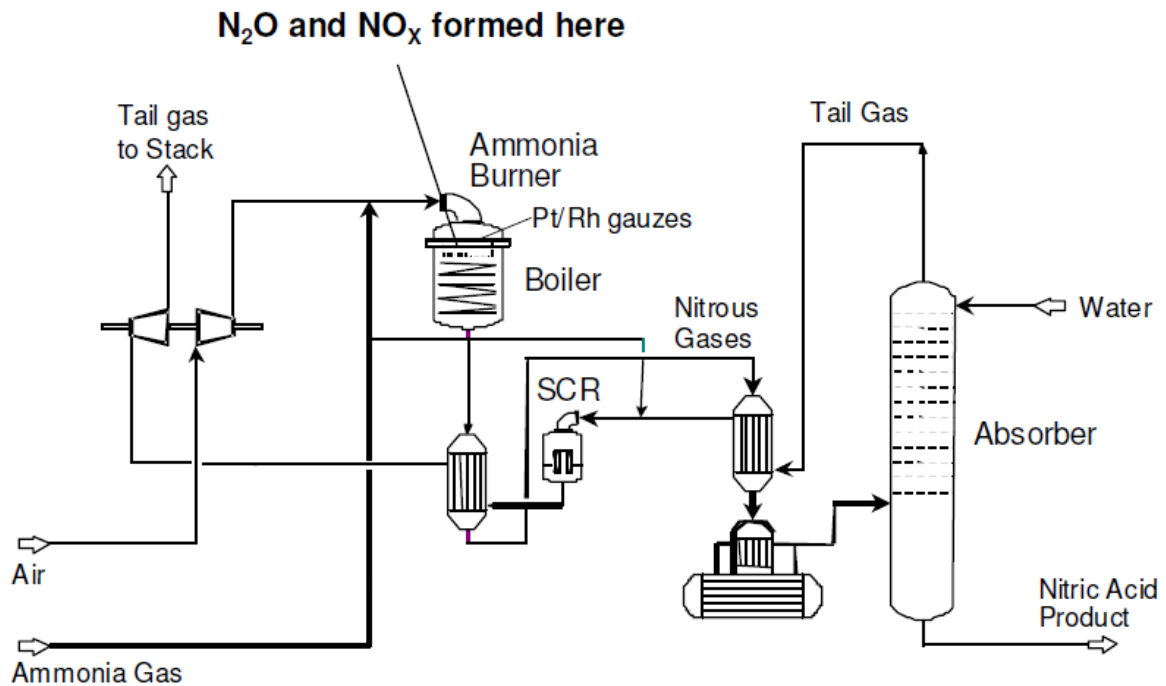


Figure 1: Flowsheet for the nitric acid process

During the water contacting step, some of the  $N_2O$  will be reduced back to  $NO$  and end up in the tail gas[6, p. 210-218]. This source of  $NO_x$  must be removed, as its release is considered unacceptable. Two main processes for catalytic  $NO_x$ -removal are currently used, selective and non-selective catalytic reduction. Older plants primarily use non-selective catalytic reduction, which helpfully remove both  $NO_x$  and  $N_2O$ . Sadly, the non-selective process is costly in energy and requires a high gas temperature. More modern plants therefore use the selective catalytic reduction[7]. Since this process does not remove  $N_2O$ , it creates a problem with  $N_2O$ -release from the plants. Very modern plants can be designed to remove the  $N_2O$  without using a catalyst by using such features such as extended hot zones, which thermally breaks down the  $N_2O$ . Modifying existing plants to any significant degree can be very expensive and there therefore exists a significant segment of plants needing a different solution. The solution offered by YARA is to place a catalyst by the platinum/rhodium gauze, in place of the usual support structure.

The catalyst offers both support to the gauze and catalytic reduction of  $N_2O$ . This allows the retrofitting of existing plants to deal with the  $N_2O$  issue fairly easily and cheaply[3].

## **2.2 Catalyst materials.**

The YARA 58-Y1 catalyst consists of two parts, an active catalyst and a support. The catalyst used is cobalt oxide  $Co_3O_4$ , where the cobalt itself exists in both the  $Co^{3+}$  and  $Co^{2+}$  oxidation forms. The cobalt oxide has a spinel structure with both octahedral and tetrahedral sites. The  $Co^{3+}$  occupies the octahedral sites, while the  $Co^{2+}$  occupies tetrahedral sites[8]. The structure allow for substitution of cobalt with materials such as iron[9] and aluminium[10]. While the two oxidation states of iron allows it to occupy both sites, though it prefers tetrahedral sites when iron is less than one third of total metal atoms, aluminium will occupy octahedral sites. The purpose of adding aluminium is to increase the surface area of the catalyst particles and stabilize the cobalt oxide. As the catalyst is used, cobalt will evaporate and increase the relative aluminum concentration in the catalyst and stabilizing it[11]. The final catalyst uses around 2% cobalt aluminate with a formula of  $Co_2AlO_4$  as its active phase, with the remaining being the support material.

The catalyst may use both magnesium oxide and cerium oxide as a support. Magnesium oxide is inert in the catalytic reaction, but has the downside of cobalt being transported into the magnesium oxide structure during use, leading to lower activity. Cerium oxide and cobalt oxide are not soluble and will not mix during use[12]. Cerium oxide is not inert in the reaction and has catalytic activity in the reaction. It also interacts with the cobalt oxide in interesting ways, affecting oxidization of the cobalt ions. The grade of cerium oxide used has significant effect on the activity of the final catalyst, as shown in Figure 2: Different grades of cerium oxide and their effects on catalyst performance.[3].

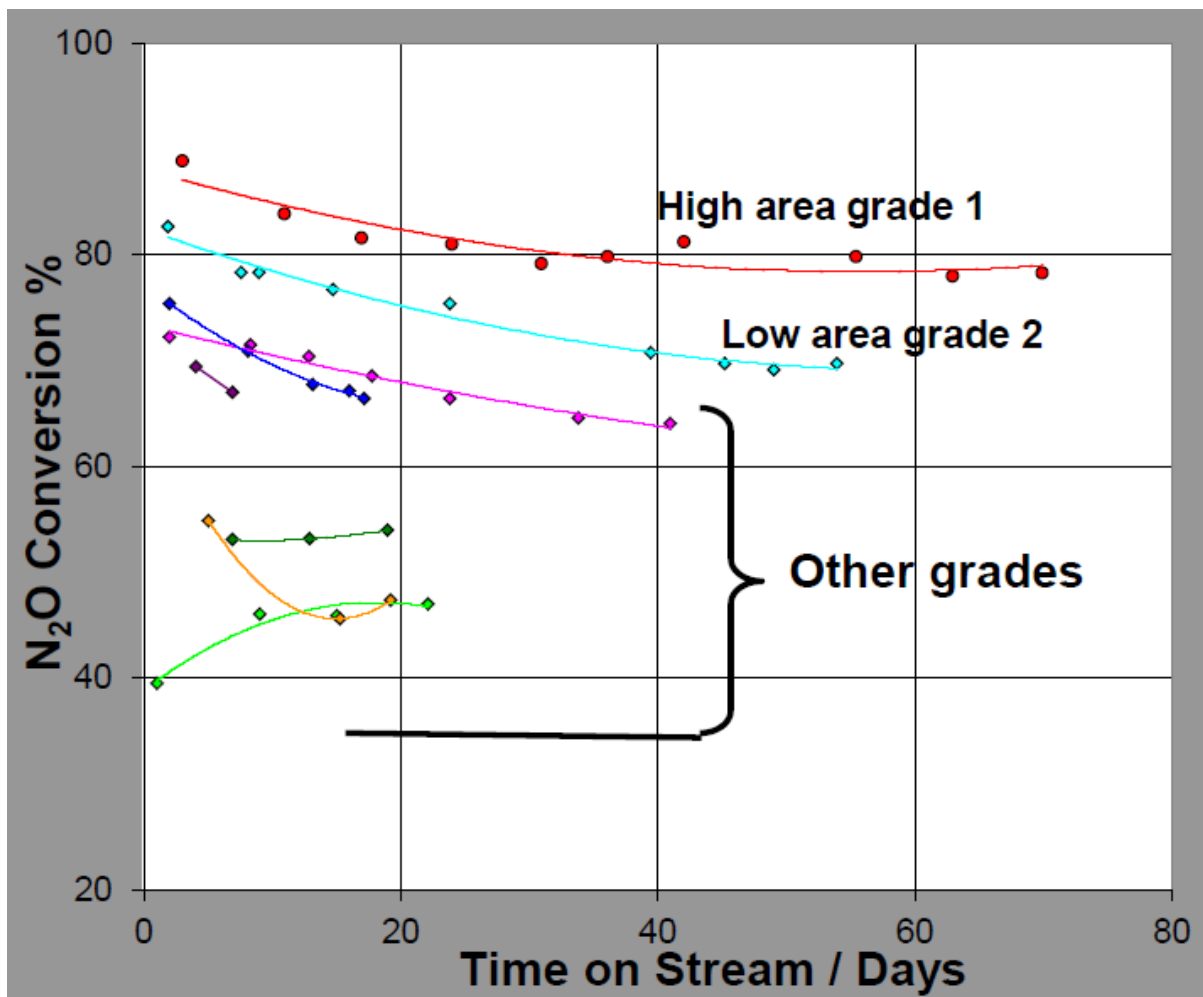
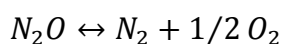


Figure 2: Different grades of cerium oxide and their effects on catalyst performance.

The catalyst based on the high surface cerium oxide starts with, and maintains a higher performance than the low surface one. The deactivation shown is primarily due to settling of the catalyst pellets causing a free space between them to lower and performance to drop. The answer to this is to fill the space created with more catalyst, increasing total conversion. The high area grade cerium oxide is a grade often used for catalytic converters in cars, while the low area grade has a more muddy origin. Properties, such as whether the oxide is acidic or basic, do not appear to be predictive for performance[13].

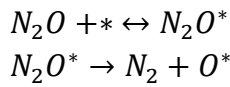
### 2.3 Reaction and mechanism

The function of the 58-Y1 catalyst is facilitate the reduction of  $N_2O$  to nitrogen and oxygen though the reaction seen below[14].

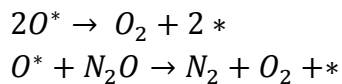


This reaction will happen by itself around 900K, but is sped up when a catalyst is used. The mechanism for the catalytic decomposition includes the adsorption of nitrous oxide, followed by decomposition and removal of nitrogen as nitrogen gas.

The bond between nitrogen and oxygen is weaker than between nitrogen and nitrogen, with an activation energy of 250-270 kJ/mol. The adsorption reaction is seen below.



Once the oxygen is adsorbed to the catalyst two different mechanisms are possible, the combination of the adsorbed oxygen with another adsorbed oxygen, or the direct reaction of nitrous oxide with adsorbed oxygen.



The mechanism dominating and the rate limiting steps vary depending on catalyst preparation and the reaction conditions. Doped  $Co_3O_4$  exhibits better performance than pure cobalt oxide and this is due to the dopants effect on the redox properties of the material. Experiments have shown that potassium increases the catalytic activity of a cobalt oxide/cerium oxide system by aiding the switch between  $Co^{2+}/Co^{3+}$  oxidation states to accommodate adsorbed oxygen and subsequent migration and desorption of the oxygen[15]. Cerium oxide itself can also act to influence the properties of the cobalt oxide. The cerium oxide and cobalt oxide phases remain separate, but the interphase between them is catalytically active in that the Co-O bond becomes elongated due to the interaction with ceria, therefore being more easily broken[12]. Another factor influencing the activity of the catalyst is the surface area of the catalysts[15]. The substitution of aluminium into the structure serves to increase the surface area of the catalyst, increasing activity up to a certain point. The effect of this can be seen in Figure 3[10].

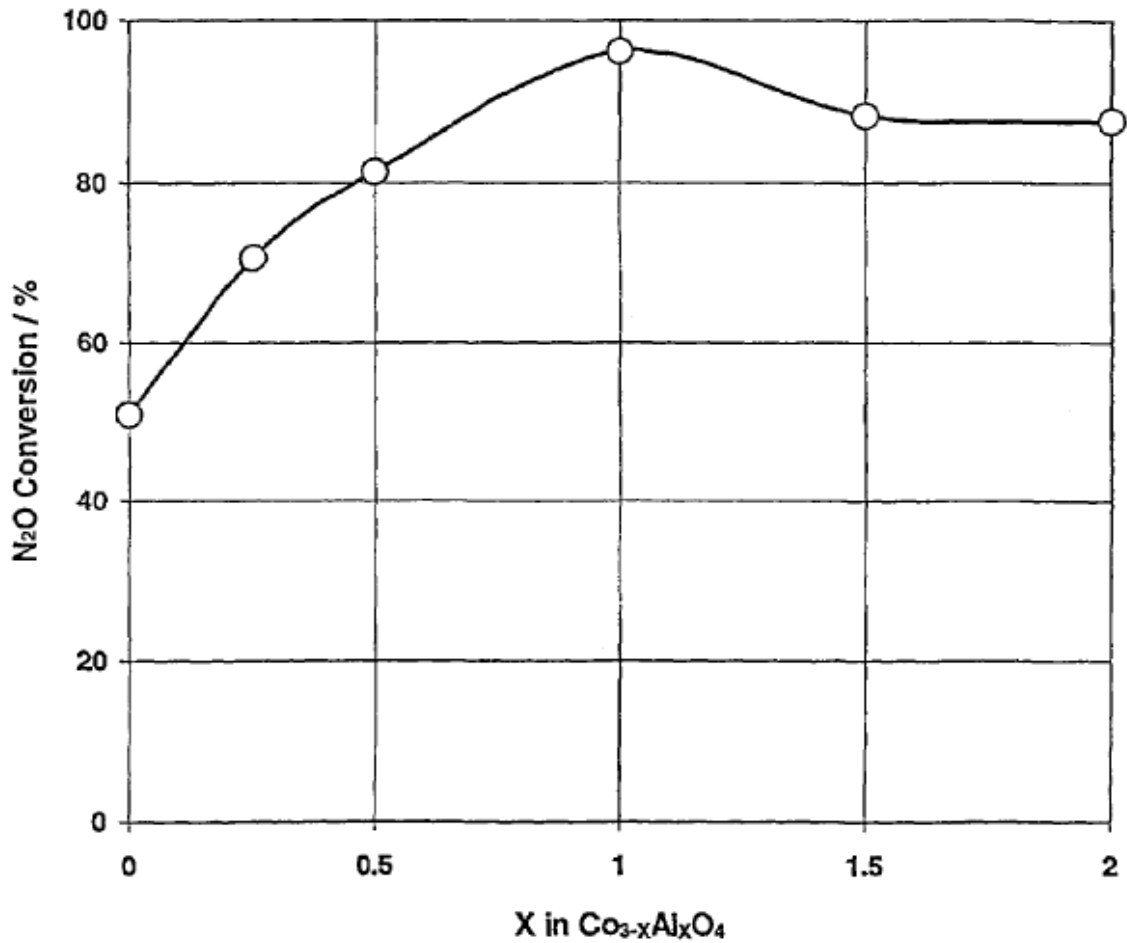


Figure 3: Aluminium content and its effects

Beyond just increasing the surface area of the active catalyst, aluminium serves to stabilize the cobalt to avoid reduction to CoO. The Yara 58-Y1 catalyst uses around one weight percent cobalt oxide and one weight percent cobalt aluminate to create a final active material with a formula of  $\text{Co}_2\text{AlO}_4$ . The rest of the catalyst is cerium oxide[10, 16]. At high temperature and in a stream containing only  $\text{N}_2\text{O}$  and Argon,  $\text{Co}_3\text{O}_4$  is reduced to CoO while in a stream containing oxygen it remains as  $\text{Co}_3\text{O}_4$ . In the cerium oxide/cobalt oxide system, the interphase becomes more important as the amount of cobalt decreases, while  $\text{Co}_3\text{O}_4$  becomes more active when the cobalt content increases. Ewa Iwanek et al. found that whether oxygen was in the stream did not affect activity for a cobalt content below 64%, implying that the interphase is the most important catalytic factor for a catalyst with only 2% cobalt[12].

From the original patent there is a graph comparing the performance of various cobalt oxide amounts and supports, seen in Figure 4.

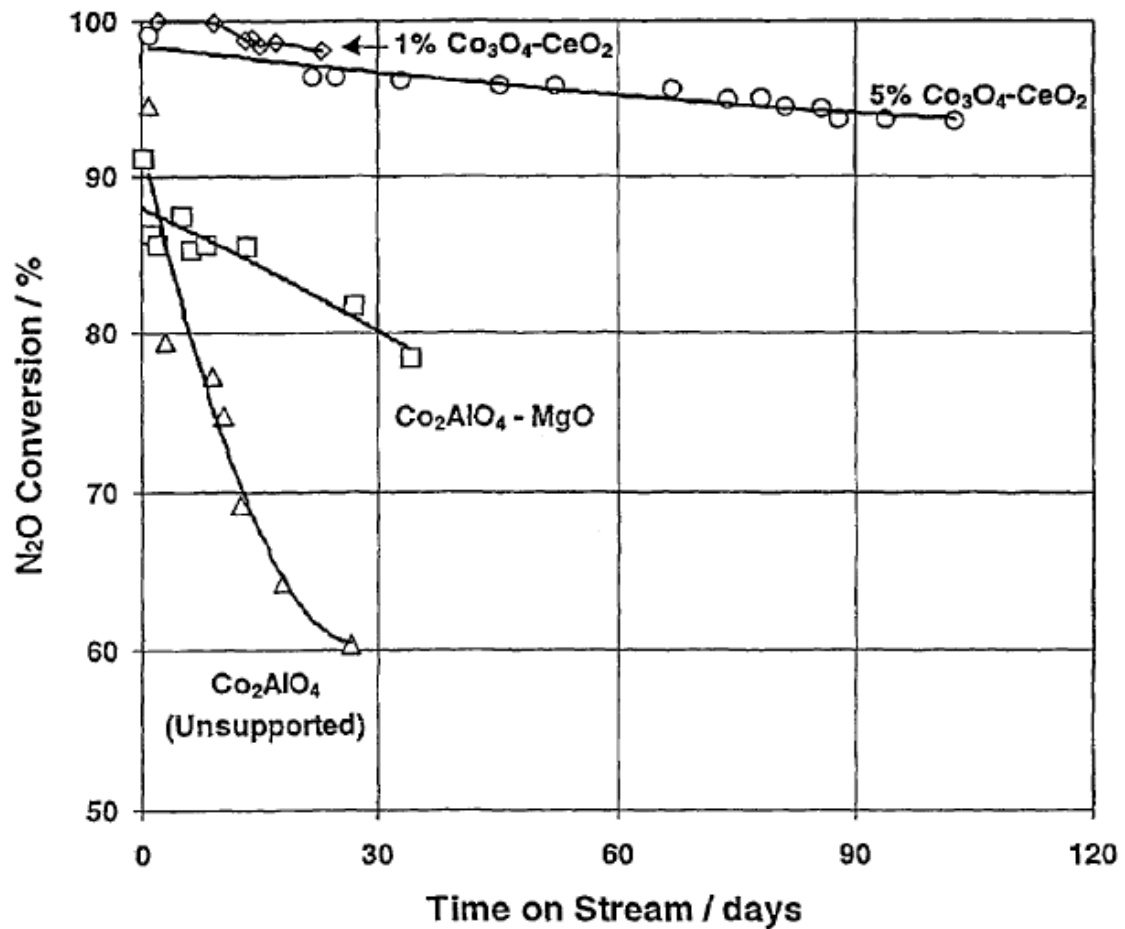


Figure 4: Comparisons between different amounts of cobalt oxides and supports

From this it would seem that a catalyst using a magnesium oxide support would be of lower activity than a cerium oxide support, indicating that interaction between the cobalt oxide and the cerium oxide helps, but does not entirely dominate the reaction, given that magnesium oxide has decent performance, at least initially. It also reinforces just how important having a support is for stability. Note that 1% cobalt oxide on a cerium oxide support appears to have a higher conversion than pure cobalt aluminate, even initially before deactivation.

The effect of catalyst loading on performance is seen in Figure 5.

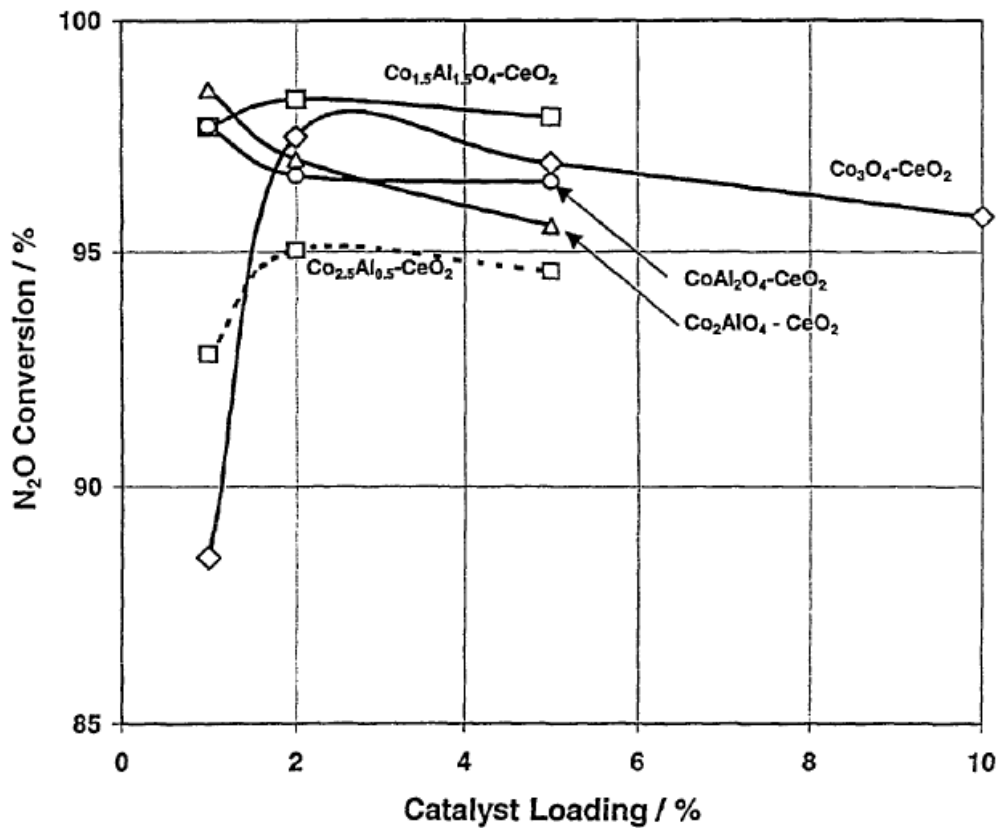
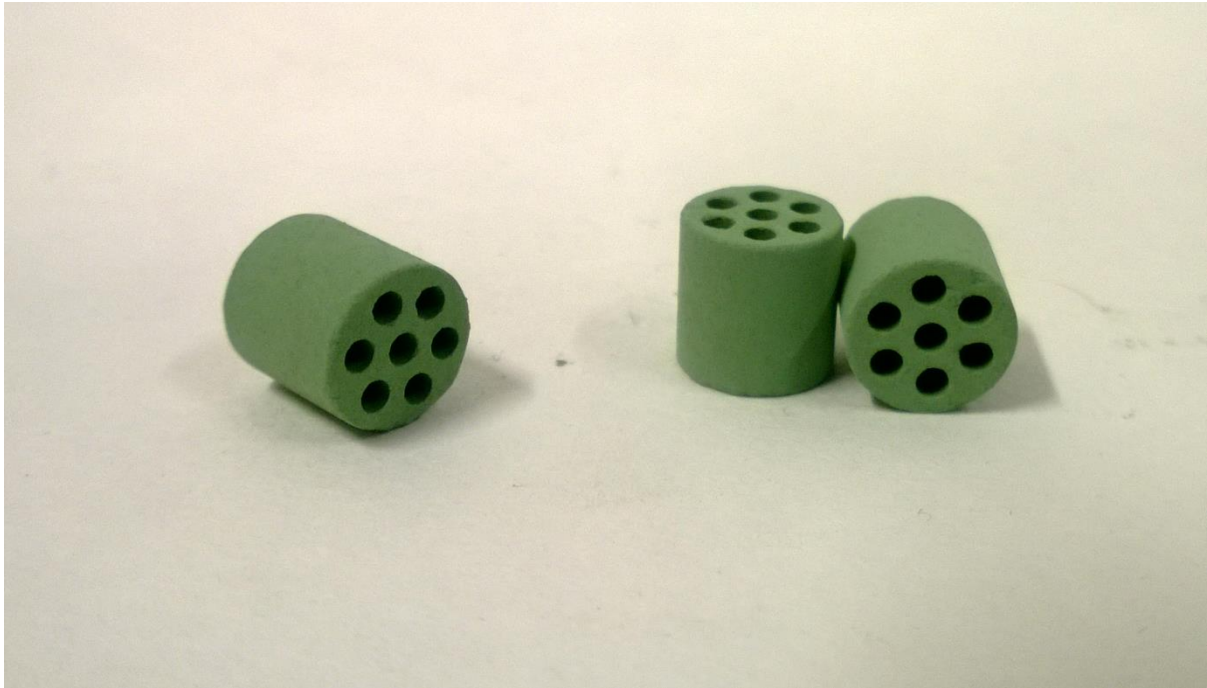


Figure 5: Catalyst loading and its effect on performance

From this figure, it can be seen that adding more of the active material to the catalyst is actually detrimental to performance, cementing the importance of the support material.

#### 2.4 Catalyst preparation

The first step in making the catalyst is to make a slurry out of the cerium oxide and the cobalt and aluminium precursor salts before milling the particles from  $25\mu\text{m}$  to  $1\mu\text{m}$ . During this milling, organic processing aids and pore formers are added. The aim of the pore formers is to create macropores in the catalyst to increase surface area. The slurry is then degassed. The next step is spray drying with the aim of getting round, dense granules. Finally the spray-dried granules are pressed into pellets[3]. Once the pellets have been pressed, they are calcined at  $980^\circ\text{C}$  for 12 hours. Finished catalyst pellets are shown in Figure 6.



*Figure 6: Catalyst pellets*

## **2.5 BET**

BET (Brunauer, Emmet and Teller) analysis is a way of investigating the surface area and the pores of sample particles. This is done using an inert gas that adsorbs non-specifically on the surface of the particles. This is in contrast with chemisorption, where the adsorption happens strongly at specific sites. BET analysis therefore gives the total surface area of the particles as compared to the amount of catalyst sites for chemisorption. A common adsorption gas is nitrogen, which takes up an area of  $16,2 \text{ \AA}^2$  per adsorbed molecule at the adsorption temperature of 77 K. Since the area per amount gas adsorbed is known, the surface area can be found directly from the amount of gas adsorbed. A complicating factor is that physisorption can be multi-layered and that gas will condense in pores.



A possible isotherm is shown in Figure 7.

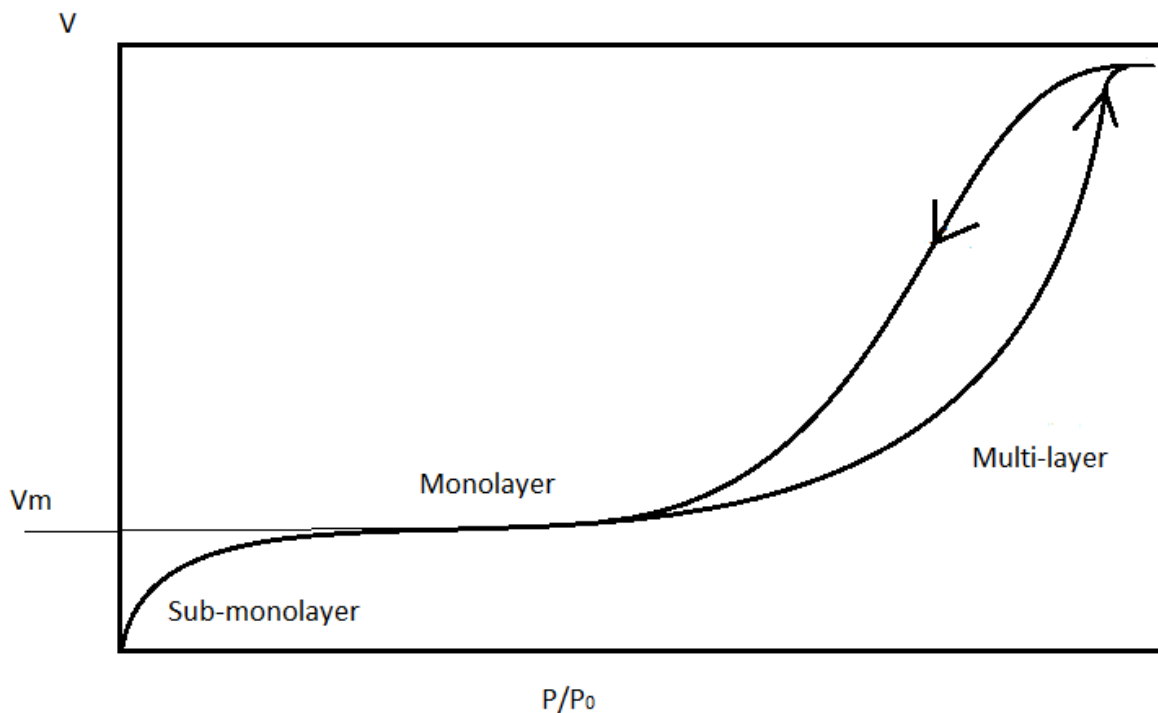


Figure 7: A BET adsorption isotherm, also showing a hysteresis loop

A BET adsorption isotherm will typically rise at the start as gas is adsorbed, before flattening at monolayer coverage. As the nitrogen pressure increases, the nitrogen will start multi-layer adsorption and pore condensation. A hysteresis loop may result from the capillary condensation. [17, p. 185-190]. The BET equation is seen below[18].

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

P is the partial pressure of nitrogen,  $P_0$  is the saturation pressure, V is the volume of nitrogen adsorbed at P,  $V_m$  is the volume adsorbed at monolayer coverage and C is a constant. Plotting  $P/V(P_0 - P)$  versus  $P/P_0$  gives  $(C-1)/V_m C$  as the slope and  $1/V_m C$  as the intercept. The equation gives best results at pressures between 0,05 and 0,3  $P/P_0$

## 2.6 XRD

XRD (X-ray diffraction) is a way of identifying crystalline phases and to gain indications of particle size in a sample by using X-rays. When the X-rays hit the sample, they are scattered elastically by the atoms in the particles. Monochromatic X-rays that are in phase will create constructive interference and create a diffraction pattern. The X-rays are sent to the samples over a range of angles and the interference will happen at certain angles dependent on the structure of the sample and will show up as peaks in a plot of signal to angle.

By measuring the angles ( $2\theta$ ) where the interference is constructive, the lattice spacing may be derived using the Bragg relation as shown below.

$$n\lambda = 2d\sin\theta, n = 1, 2, \dots$$

In this equation,  $\lambda$  is the wavelength of the X-ray,  $\theta$  is the angle between the incoming X-ray and the normal to the reflecting lattice.  $d$  is the distance between two lattice planes, while  $n$  is the order of reflection (an integer). The reflection is shown in Figure 8.

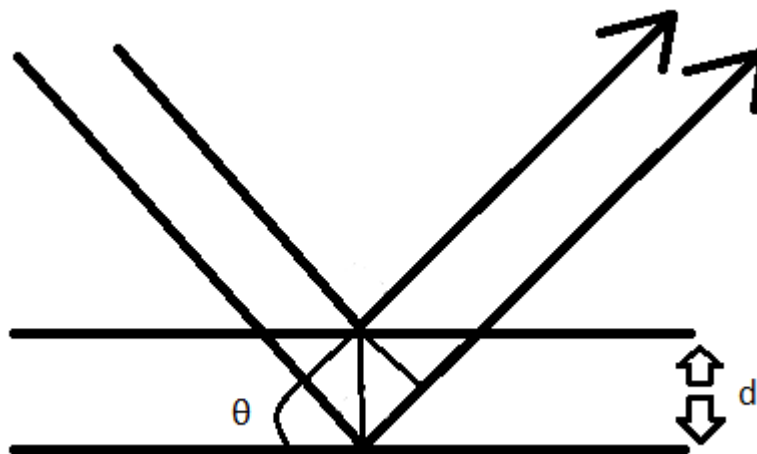


Figure 8: Reflectance of X-rays

The lattice spacings are characteristic of compounds, and phases and compounds may be identified from the different peaks in the diagrams.

Proper diffraction is dependent on the long range ordering of the sample. This dependency can be used advantageously to gain an indication of the particle size. For well-ordered crystalline samples, the peaks in the diffraction pattern are very narrow, but for crystallite sizes below 100 nm, the peaks will broaden. Usually, the photons out of phase will interfere destructively, but for the smaller crystallites, the destructive interference is incomplete.

The formula used for the calculation of particle size is the Scherrer equation, seen below.

$$\langle L \rangle = \frac{K\lambda}{\beta \cos\theta}$$

$L$  is here the dimension of the particle perpendicular to the reflecting plane, while  $K$  is a constant (usually 1) and  $\beta$  is the peak width.  $\lambda$  and  $\theta$  are as before the wavelength of the X-ray and the angle of the beam respectively.

If the crystallites are too small or too amorphous, they will not show up in the diffraction pattern, and XRD will therefore not give a complete characterization of all possible phases[17, p. 131-134]. Compounds present in small amounts such as less than one weight% may also be hard to detect[18].

When a powdered sample is used, only the crystal planes aligned such that constructive interference is created will show up and the pattern will be created by a small part of the sample. Rotating the sample during analysis will increase the amount of sample aligned correctly[17].

## **2.7 SEM**

The scanning electron microscope uses electrons shot from a filament gun to characterize a surface. The electron beam is focused by lenses to a small spot and scanning is done in a raster fashion, with an intensity given for each point. The electron beam gives rise to different signals, secondary electrons and backscattered electrons. The secondary electrons are electrons knocked off from the sample that are collected. The penetration of the electron beams created a working volume formed like a cone. The secondary electron scans give a good topographical representation of the sample. Backscattered electrons are electrons reflected off the sample. The reflection is dependent on the weight of what it hits, so the backscattered electrons can give information about the different elements in a sample. When the two scans are combined, one can see both the topography and composition of the sample[19].

### 3. Experimental

Two grades of cerium oxide, one of high surface area and one of low surface area were obtained from YARA. Catalysts based on the two grades of ceria were also obtained. The catalysts were obtained as both fresh and used samples. Cerium oxide were obtained as a powder, while the catalysts were obtained as catalyst pellets. The used pellets have been used in a plant for around three years. In order to facilitate analysis, the pellets were crushed using a mortar. High surface cerium oxide was in addition sintered at 700 °C 900 °C and 1100 °C with a one hour ramp up time and a seven hour hold time. After heating, the samples were left to cool in the oven with the door closed until the temperature was below 200 °C

#### 3.1 Surface area measurements

The surface area of all the samples were measured by BET using a Micrometrics TriStar 3020 using nitrogen adsorption. Before analysis, samples were degassed at 200 °C. Samples were weighed both before and after degassing, with the after degassing number being used for further calculations. The surface area of ground catalyst was compared to catalyst divided only just enough to fit in the sample tubes to check if the grinding significantly affected surface area. Crushed and divided catalyst is seen in Figure 9.



Figure 9: Ground and split sample

The divided catalyst was divided using a scalpel. The final pieces for analysis were around half the size shown here.

### **3.2 X-Ray diffraction**

Analysis by X-Ray diffraction was done using a Bruker AXS D8 Focus diffractometer. Analysis of the results were done using Bruker Diffrac.eva 3.2, with Bruker AXS Topas 4.2 used for fitting and calculation of crystallite size. For analysis of

### **3.3 Scanning electron microscopy**

SEM was run on a Hitachi S-5500 scanning electron microscope. Acceleration voltages were primarily 5 and 10 kV. Carbon tape was placed on the sample holder and powder transferred onto it using tweezers. Excess powder was removed with pressurized nitrogen.

## 4. Results

### 4.1 Surface area measurements

Results for nitrogen BET are summarized in Table 1, with a cerium oxide grade and the unused and used catalyst based on it shown along the same row.

Table 1: BET results

Sample	Cerium oxide powder [m <sup>2</sup> /g]	Unused catalyst [m <sup>2</sup> /g]	Used catalyst [m <sup>2</sup> /g]
High surface	110,2	4,6	2,3
Low Surface	5,5	1,4	1,3

From the table it is evident that the high surface grade cerium oxide does indeed have a significantly higher surface area than the than the low surface area catalyst. It is also evident that loss of surface area is significant during catalyst preparation. The catalyst based on the high surface area grade cerium oxide retains a significant lead in surface area. It is also interesting to note the loss of surface area in the used catalyst for the high surface area grade catalyst. There is no real loss for the low surface area grade, though this might well be due to the sample having a total surface area well below the accuracy limit for nitrogen BET.

Of some further interest are the sample pores, summarized in Table 2.

Table 2: Pore volumes and sizes

Sample	Pore volume [cm <sup>3</sup> /g]	Average pore size [Å]
Cerium oxide, High area	0,158	59,01
Cerium oxide, Low area	0,0181	124,44
Catalyst, High area unused	0,0092	74,32
Catalyst, Low area unused	0,0026	78,70
Catalyst, High area used	0,0036	60,83
Catalyst, Low area used	0,0021	62,70

The difference in pore structure is significant between the high and low surface ceria with the high surface having a much higher pore volume. The curves indicate cylindrical pores in the high area grade, but a more clay-like structure in the low area grade. A comparison between the adsorption-desorption curves can be seen in the appendix. Once the materials have been made into catalysts, mesopores have more or less disappeared. The observed pore volume correlates with observed surface area, with a higher surface area correlating with a higher pore volume.

In order to see the effect of heat on the cerium oxide, high surface ceria was sintered at 700, 900 and 1100 °C. The results are seen below in Table 3.

*Table 3: Sintered ceria*

High surface ceria	Surface area [m <sup>2</sup> /g]	Pore volume [cm <sup>3</sup> /g]	Pore size [Å]
Standard	110,2	0,158	59,01
700 °C	62,1	0,155	98,5
900 °C	21,8		
1100 °C	6,6	0,0146	88,6

For the ceria sintered at 1100 °C, significant differences between adsorption (shown) and desorption are present, but the pore volume is very small regardless. Significant reduction in surface area can be seen even after 700 °C. In comparison, the catalyst is calcined at 980 °C for 12 hours.

## 4.2 X-Ray diffraction

The XRD-results were processed using both Bruker diffrac.eva and Topas. Crystallite sizes were obtained from fitting the results in topaz and from scherrer analysis in .eva. Both integral and full width at half maximum methods were used in both cases. For the eva analysis, only the first peak was used. Since the cerium oxide crystals are cubic, they have only one parameter, which was also obtained through topas fitting. The crystallite sizes for cerium oxide and the cerium oxide parts of the catalysts are shown below in Table 4.

*Table 4: Cerium oxide crystallite sizes*

Sample	a [Å]	Lvol-IB [nm]	Lvol-FWHM [nm]	Scherrer IB (First peak) [nm]	Scherrer FWHM (First peak) [nm]
Cerium oxide, High area	5,4121	6,48	8,00	8,65	9,44
Cerium oxide, Low area	5,4123	52,02	72,72	52,31	66,48
Catalyst, High area unused	5,4121	67,32	85,28	61,05	71,21
Catalyst, High area used	5,4113	79,77	99,01	70,21	81,95
Catalyst, Low area unused	5,4117	92,68	113,07	78,64	89,01
Catalyst, Low area used	5,4112	95,44	112,11	78,59	88,63

Crystallite size is significantly smaller for the high-surface ceria compared to the low surface ceria. Crystallite size increases when the material is made into a catalyst. For the high area catalyst, the crystallite size increases with use, while for the low area catalyst, there is little difference. This correlates with the surface area seen in Table 1.

For analysis of the cobalt oxide part of the catalysts, the results were too weak to fit properly in topaz and only one peak was to any degree visible in the results. Proper comparison between them would be hard, though sizes were generally in the area of 60-80 nm. The strength of the cobalt peak was fairly similar between unused high and low surface catalysts. This can be seen in Figure 10.

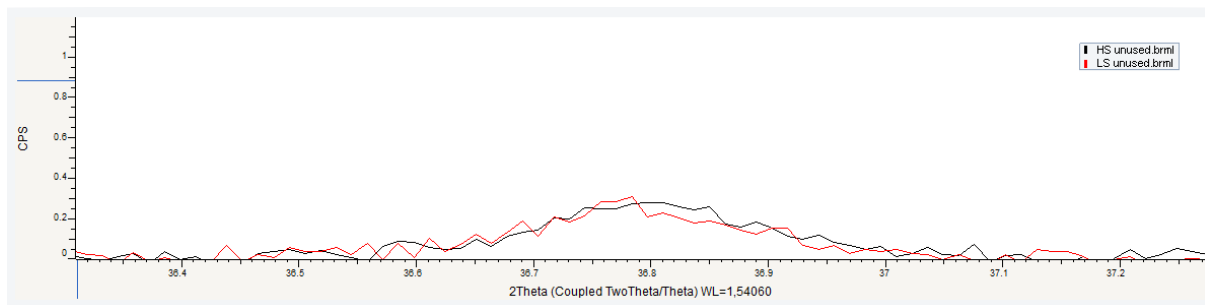


Figure 10: Normalized peaks for Cobalt oxide

Note the rather significant amount of noise in this result.  $K\alpha_2$  has not been stripped in this figure, and doing so makes the result even more of a mess. There were no significant differences in phases between the high surface catalyst and the low surface one, see appendix.



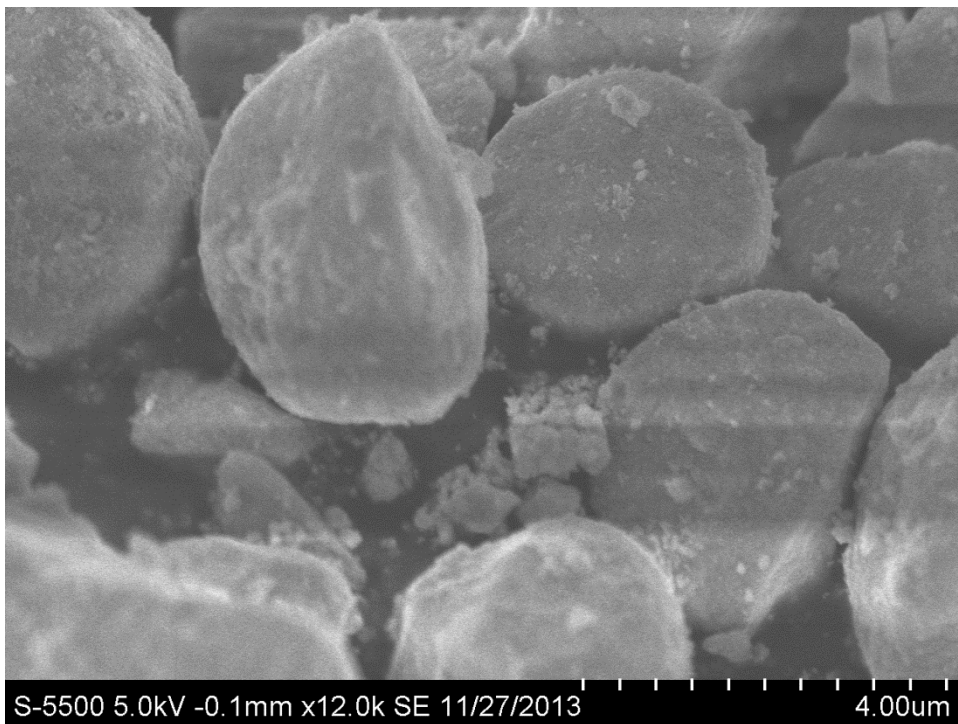
### 4.3 Scanning electron microscopy

All samples were studied under SEM.

Figure 11 and Figure 12 shows the **high surface cerium oxide** at high and low magnification respectively.



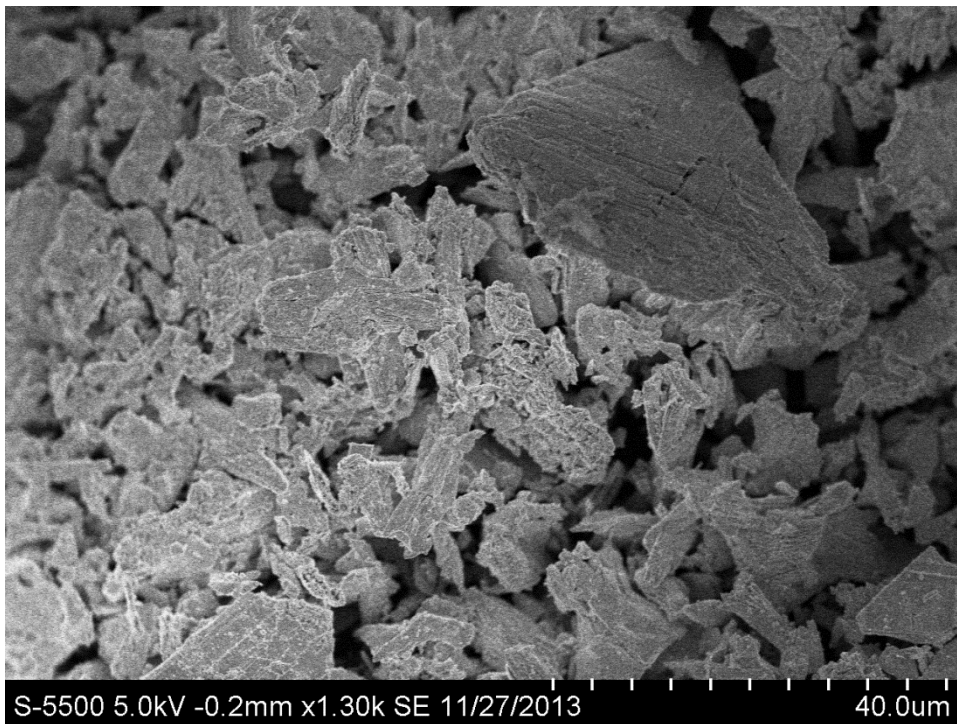
*Figure 11: High surface cerium oxide at low magnification*



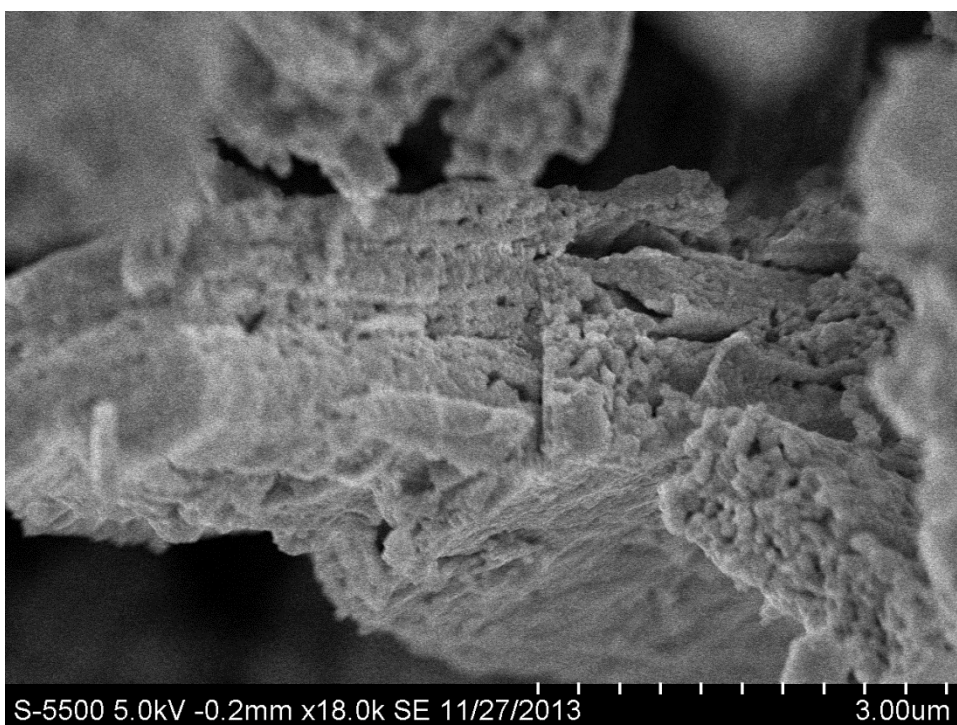
*Figure 12: High surface cerium oxide at higher magnification*

As can be seen, the high surface cerium oxide has fairly smooth and round particles.

Figure 13 and Figure 14 shows the **low surface cerium** oxide at high and low magnification respectively.



*Figure 13: Low surface cerium oxide at low magnification*

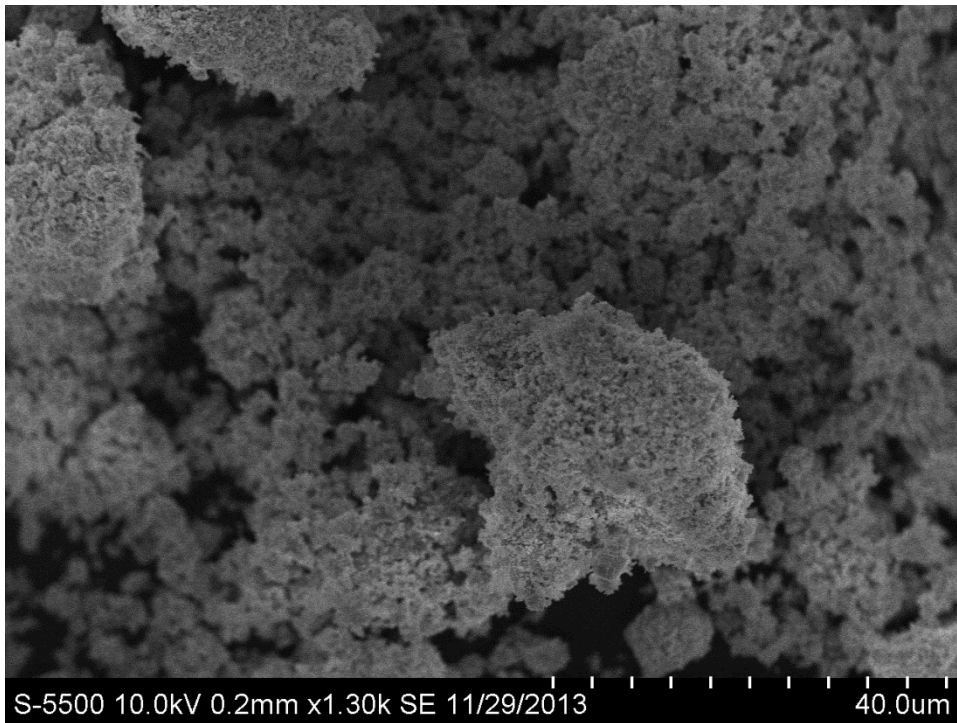


*Figure 14: Low surface cerium oxide at high magnification*

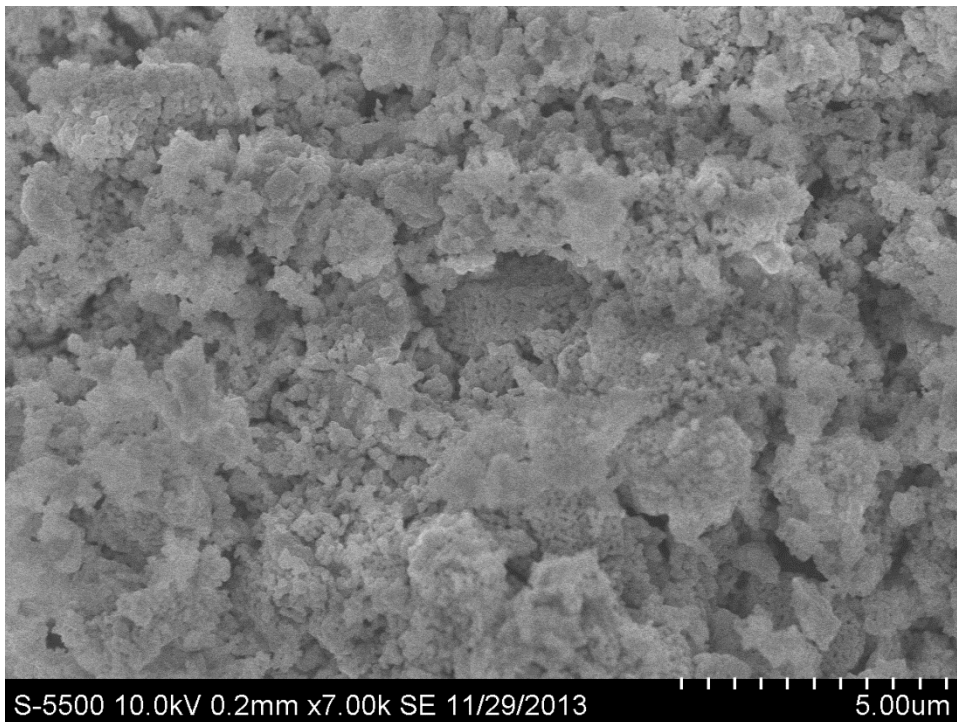
Note the significant differences from the high surface cerium oxide. The low surface cerium oxide has what looks like an almost fiber-like structure with the “fibers” built up from small round particles.



Figure 15 and Figure 16 shows **the high surface catalyst** at high and low magnification.



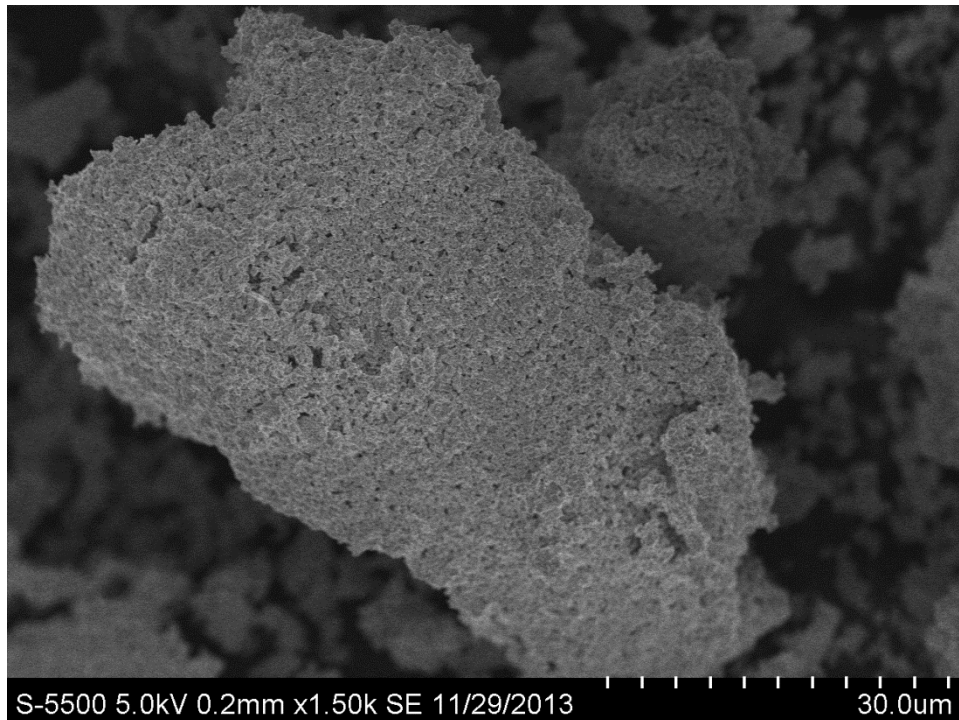
*Figure 15: High surface catalyst at low magnification*



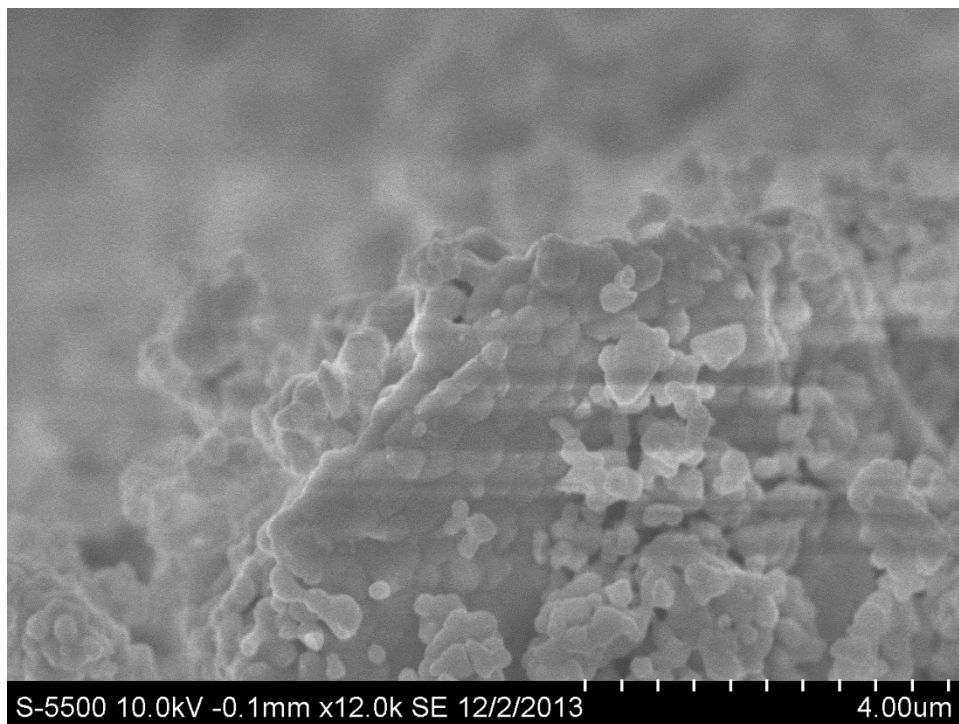
*Figure 16: High surface catalyst at high magnification*

The structure of the catalyst differs markedly from the structure of the cerium oxide, being bound in a more sheet-like structure.

Figure 17 and Figure 18 shows the **Low surface catalyst** at low and high magnification respectively.



*Figure 17: Low surface catalyst at low magnification*



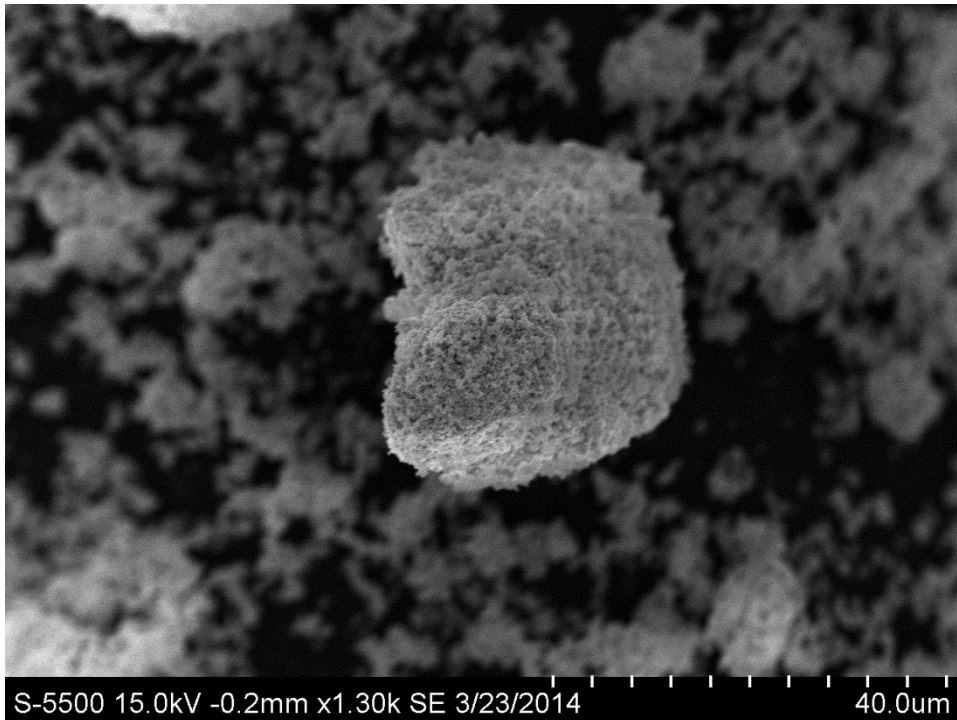
*Figure 18: Low surface catalyst at high magnification*

The finished catalysts appear to have a mix of somewhat chaotic ordered regions and tightly bound sheets.

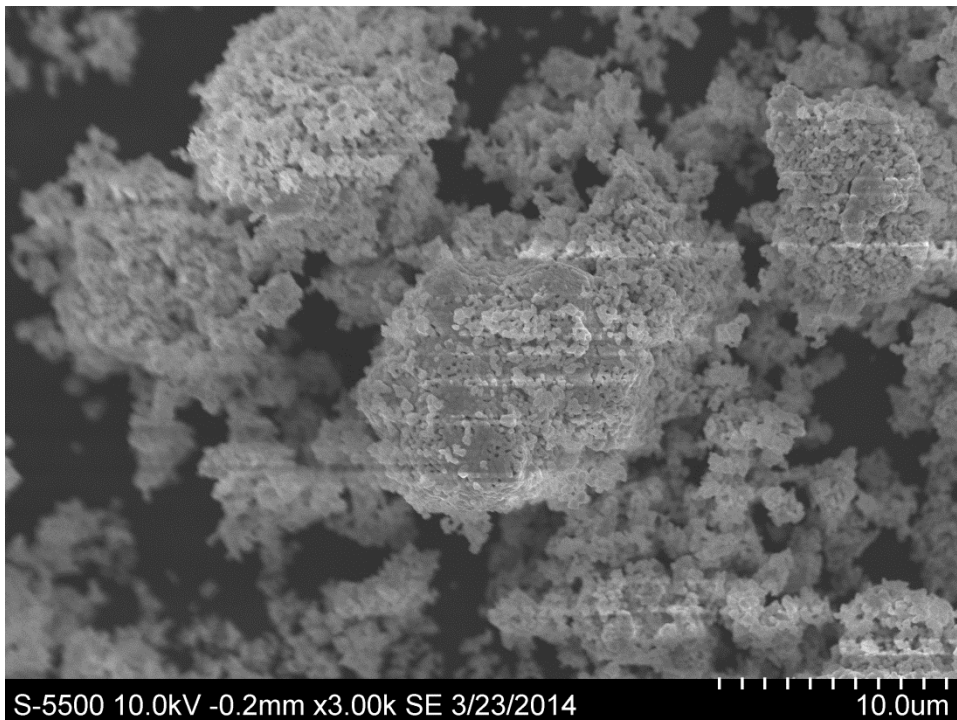


The sheets in the low surface area catalyst appear more tightly bound, though the catalysts are not homogenous in structure and one can find examples of both types of sheet in both the high and low surface catalyst. Some examples are included in the appendix.

Figure 19, Figure 20, Figure 21 and Figure 22 shows different aspects of used high surface catalyst.



*Figure 19: Used high surface catalyst at high magnification*



*Figure 20: Used high surface catalyst showing the solid sheets*

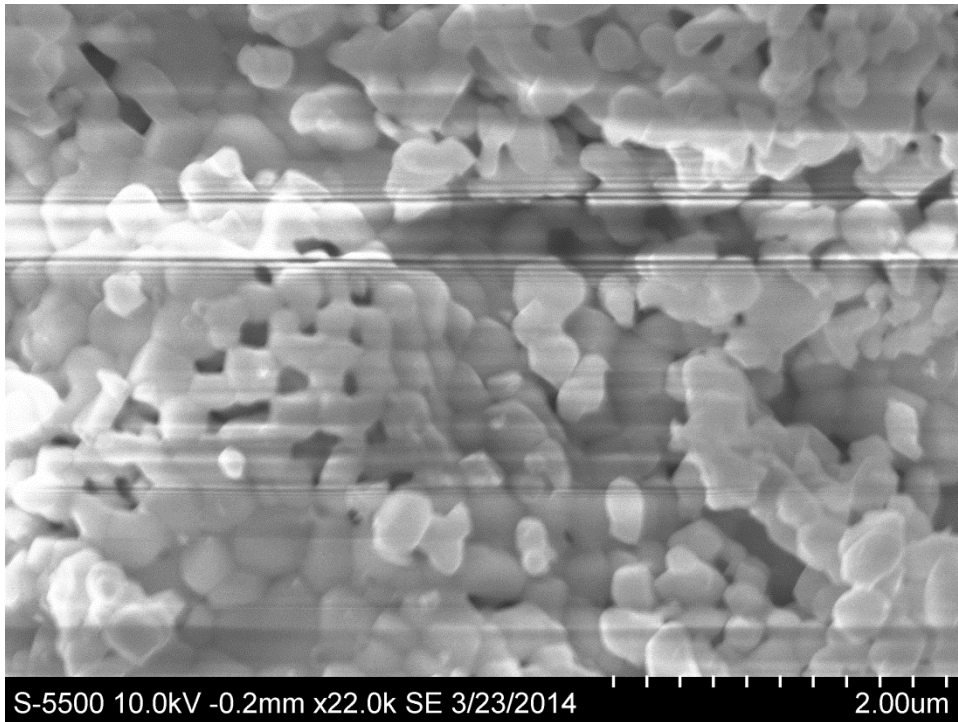


Figure 21: Used high surface catalyst showing the sheet in more detail

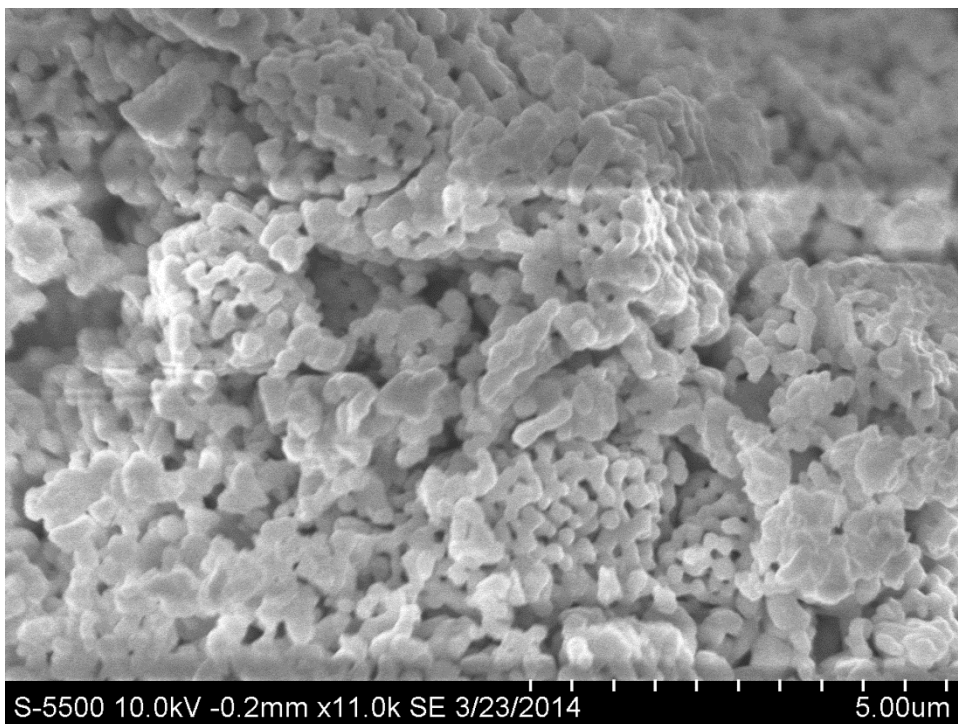


Figure 22: A more amorphous part of the high surface catalyst, with looser sheets

Again, both types of sheet is present, though the particles appear to have become more solid in the used high surface catalyst. Particle size appears larger for the used catalyst, consistent with XRD results.



Used low surface catalyst is shown in Figure 23, Figure 24 and Figure 25

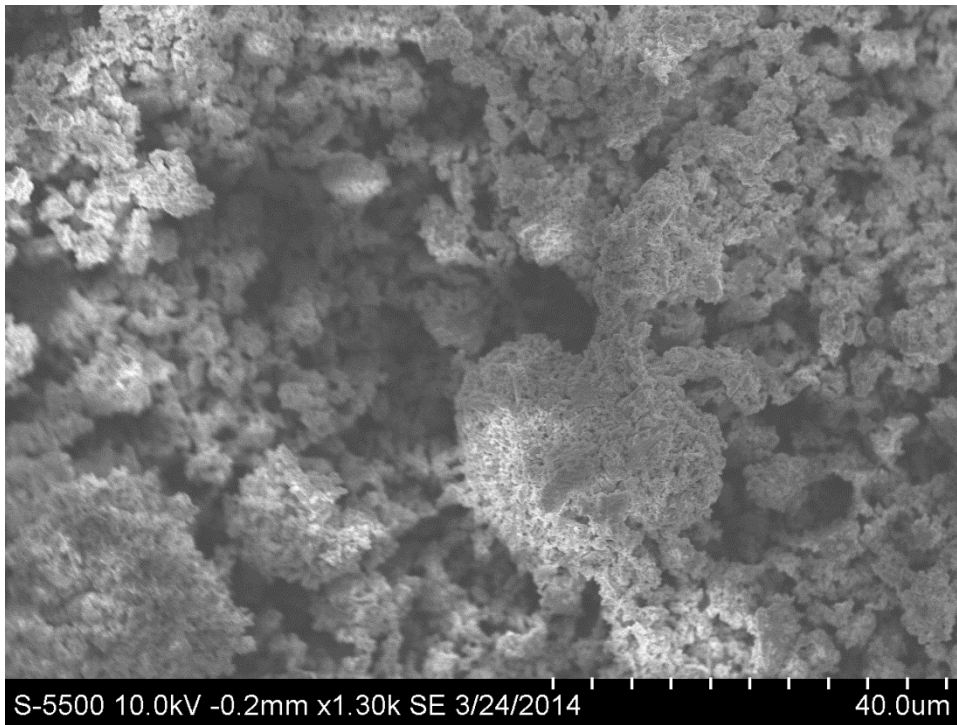


Figure 23: Used low surface catalyst at high magnification

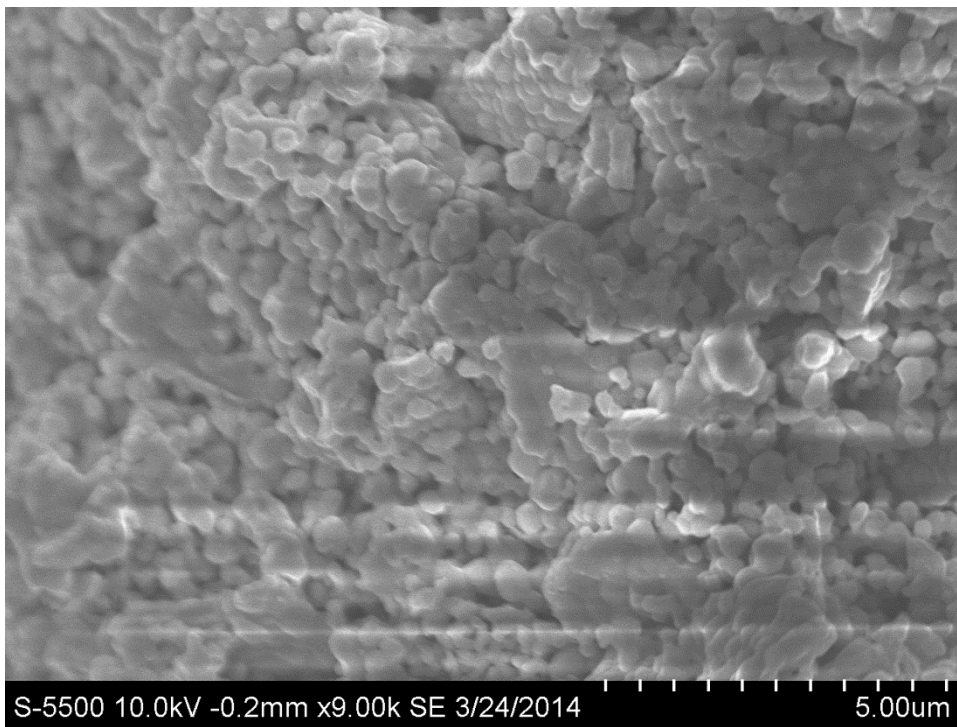
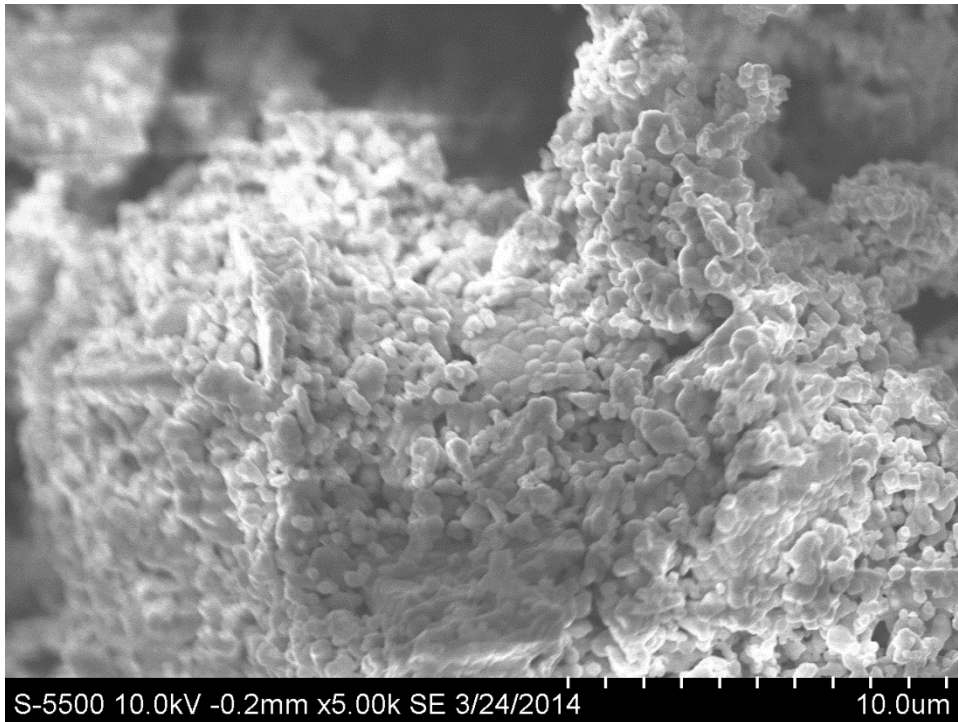


Figure 24: Used low surface catalyst showing small sheet pieces with freerer particles



*Figure 25: Another image of the used low surface catalyst showing the mix of sheets and more chaotic particles*

The low surface catalyst appears fairly similar between its used and unused samples, with small sheet pieces and more free regions. The high surface catalyst appears to have become more solid, with more dense sheets, though there are plenty of freer regions.



## 5. Discussion

Results show a dramatic decrease in both surface area and pore volume once the two cerium oxide grades are made into catalysts. This is not entirely unexpected since the catalyst preparation process involves both significant milling as well as calcination at 980 °C for 12 hours. Results do indeed indicate noticeable loss of surface area for a cerium oxide sample from a mere 700 °C for 7 hours. The catalysts do appear to be fairly tightly packed and crystalline. The catalyst preparation process uses starch to create macro-pores in order for more catalyst to be exposed to the process. This would seem a good idea, since the meso-pores are more or less wiped out during the catalyst preparation process. Some traces of the macro-pores are visible in SEM, but would not be picked up in BET. Results are consistent over several methods showing that the high surface catalyst undergoes visible changes during use, while the low surface catalyst does not. Because neither catalyst deactivates much beyond the physical reduction of free space that happens when the catalyst pellets settle and the gradual evaporation of cobalt, this would indicate that the structural changes do not to any large degree affect performance. This again would indicate that properties existing before or during catalyst preparation are responsible for the performance gap. The crush strength of the high surface catalyst pellets are 30 N, but 15 N for the low surface catalyst. This indicates significant structural differences after preparation of the catalyst.

From the work of Ørjan it is known that the cobalt aluminate particles exist as somewhat spherical mono-crystalline particles on the cerium oxide support that are flattened in the contact point. The particles have a size range of 20 nm to above 100 nm, but are typically in the region of 70 nm. Any size difference in cobalt aluminate particles between the different catalysts are hard to discern. The rather large particles scattered around the cerium oxide indicates a somewhat poor dispersion, and David Waller did indeed confirm a dispersion problem on the low surface cerium oxide. TEM results are consistent with other results in that cerium oxide particle size increases for the used high surface catalyst, though not noticeably for low surface catalyst[20].

From literature it is known that surface area of a cobalt-oxide/cerium oxide system does affect performance of the catalyst. It is further known that the interphase between the cobalt oxide and the cerium oxide can have significant effect on its own and that preparation method affects the final product significantly. It is possible that the high surface cerium oxide provides an attachment giving a better contact surface on creation of the catalyst. This would explain the lack of deactivation, as the contact area would be fixed at catalyst creation. It is also possible that the dispersion is different, though the XRD results indicate that the cobalt aluminate phases in both catalysts are fairly similar.

One possibility is that the performance difference doesn't lie with the cobalt aluminate/ cerium oxide at all, but is simply due to different pellet structure affecting performance by affecting the flow of gas through the pellet. Given that crush strength should lower with increased porosity, one would then expect the low surface catalyst to be more porous. Given that all testing was done on powder, this is hard to say. It is important to remember that studies were done at room temperature, and that the catalysts may look different during operating condition.

In analysis of XRD-results, significant influence from sample displacement was found, on the order of 30-50%, even within the 0,1 mm limit stated as acceptable. This is larger than the variation between samples and the quantitative results are therefore somewhat questionable. Since every catalyst sample was measured four times at the stated parameters, the qualitative comparison is still valid, as samples with a close displacement could be compared and corrected for. Scherrer analysis in diffract.eva being done only on the first peak would give the crystallite size in only one plane and would be correct only if the crystallites were of a similar size in all facings. Given the variation by sample displacement, the accuracy given by a single peak still corroborates the qualitative results found by topas. Sample displacement issues were mostly encountered with catalyst powders, as they had a tendency to not want be flattened. Ethanol fixing was not done, as the small amounts of powder would have given a very weak cobalt oxide signal. In the end, the cobalt oxide signal very weak and did not give proper peaks. Analysis of several peaks gave answers in the region of 55-75 nm. This fits with crystallite sizes found by Ørjan.

Further work could be done using TEM to ascertain differences in the attachment area of cobalt aluminate particles to see if there is indeed a greater interphase to work with for the system. Furthermore, the two catalysts studied are similar in their properties, notwithstanding crush strength and the initial activity gap. It would be interesting to investigate catalysts with atypical deactivation curves, as the differences there could be easier to pick up on. Analyzing the surface areas of the catalysts with krypton adsorption would allow a more accurate picture of the low surface catalysts, as they have a very low surface area that makes nitrogen adsorption unreliable. There was sadly not enough time to do this during this project. An interesting project might to finely crush the different catalysts and place them back in a lab reactor to look at performance. This would exclude performance factors related to pellet structure and allow for a better comparison of the performance difference cause by cobalt oxide/ cerium oxide interaction.

## 6. Conclusion

Two cerium oxide grades and unused and used YARA 58-Y1 nitrous oxide abatement catalysts based on them were investigated using BET nitrogen adsorption, X-ray diffraction (XRD) and scanning electron microscope (SEM) To investigate which properties might lie behind a performance gap between them. It was found that the catalyst preparation significantly reduced the surface area and pore volume from cerium oxide to catalyst, with one being reduced from 110 m<sup>2</sup>/g to 4,3 m<sup>2</sup>/g and the other from 5,5 m<sup>2</sup>/g to 1,6 m<sup>2</sup>/g. Mesopores were essentially wiped out. XRD revealed that the two catalysts were similar in structure and phases, with the catalysts looking more like the low surface ceria than the large surface area ceria. Due to there not being a significant difference in deactivation between the high and low surface catalysts, the performance differences between the cerium oxide grades probably stems from properties before or during production. The cobalt aluminate phases were similar between the high surface and low surface catalysts, indicating no major difference in cobalt particle size. The exact reason why the high surface catalyst performs better is still unknown, but could stem from a better contact surface with the cerium oxide, given that the cerium oxide/cobalt oxide interphase itself has significant catalytic activity. Other reasons might be structural in the catalyst pellets themselves.

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### Appendix 1: Comparison of BET adsorption-desorption curves

The Adsorption/desorption curves for high surface ceria, low surface ceria and high surface catalysts are presented in Figure 26, Figure 27 and Figure 28 respectively.

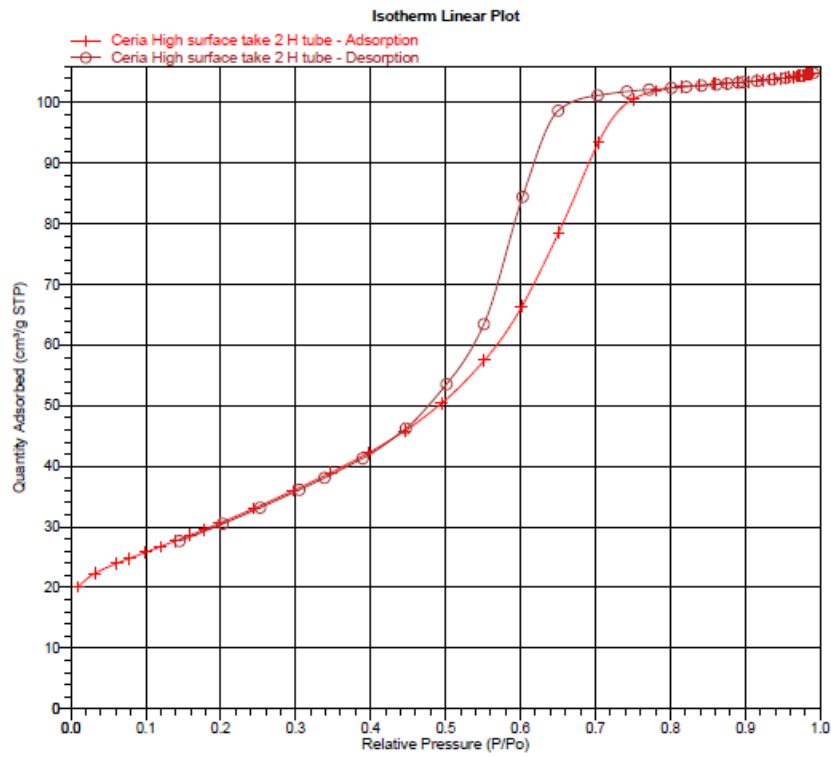


Figure 26: Adsorption/desorption curve for High surface ceria

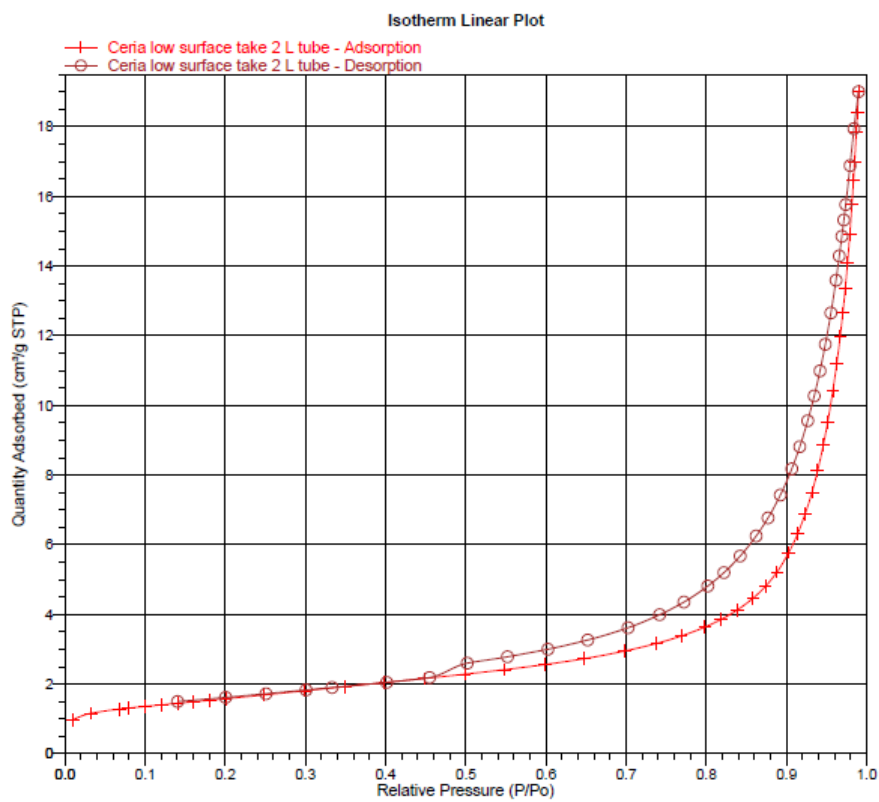


Figure 27: Adsorption/desorption curve for Low surface ceria

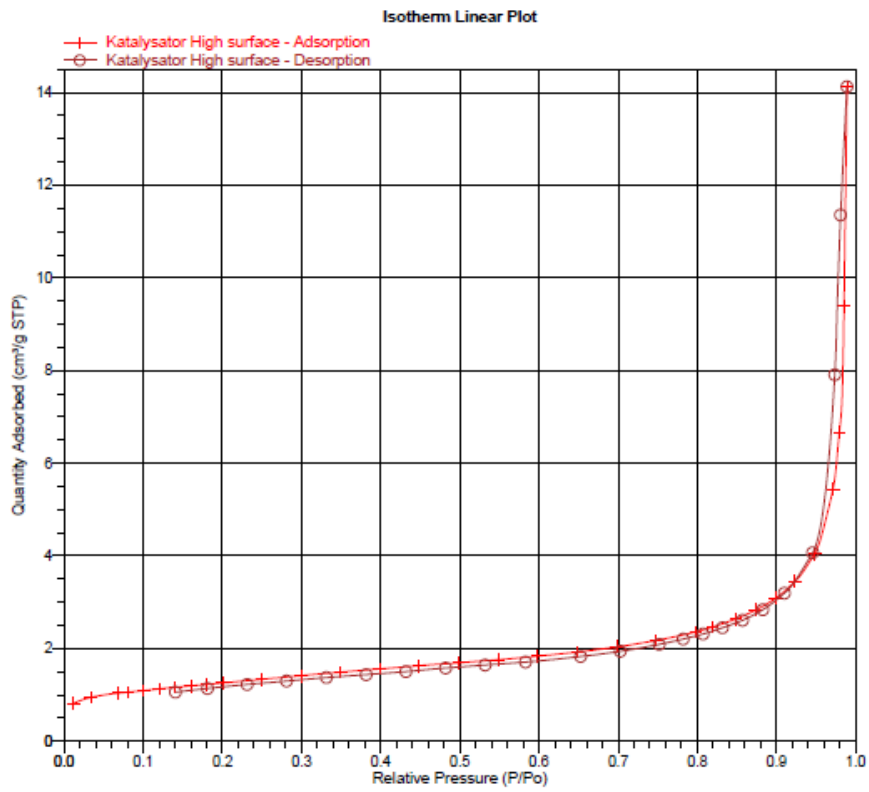
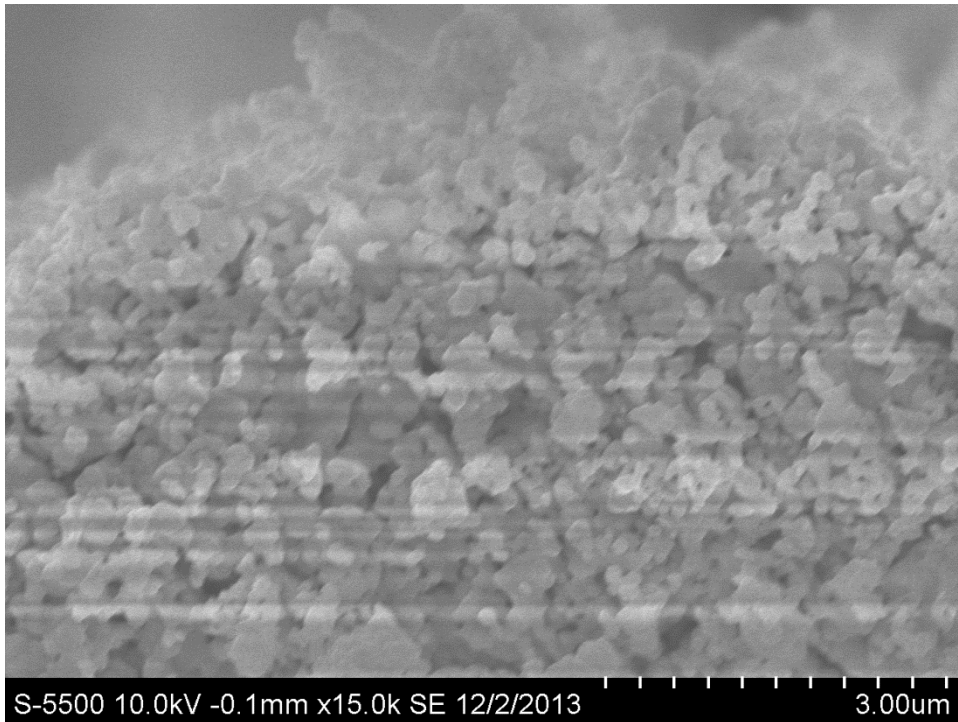


Figure 28: Adsorption/desorption curve for High surface catalyst

Note the clear hysteresis loop in the high surface ceria, this is reduced for the low surface ceria and completely disappears for the high surface catalyst.

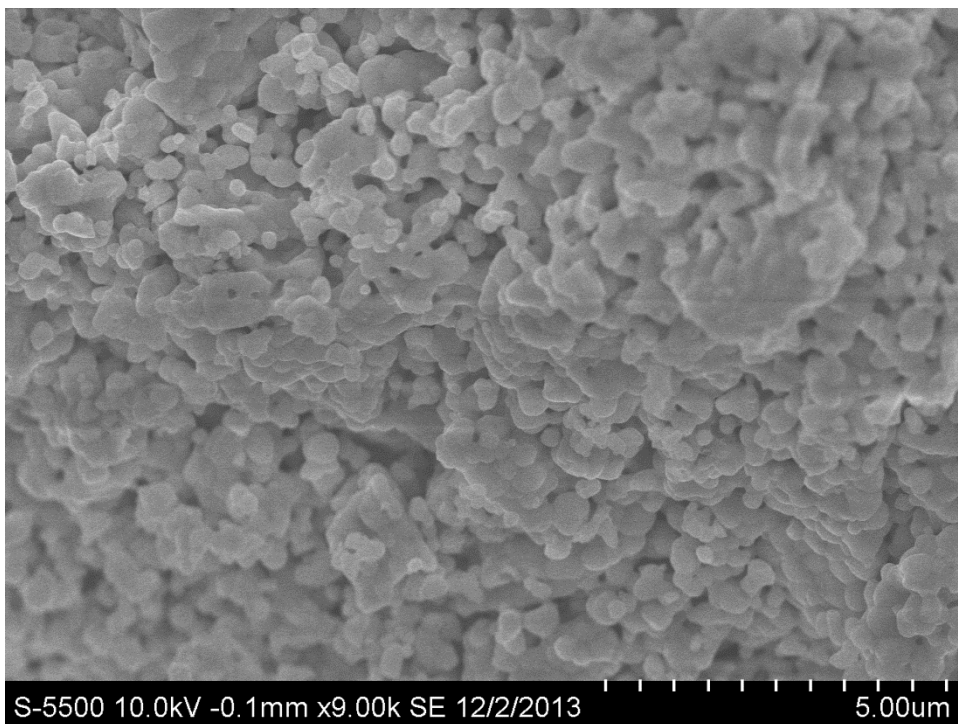
## Appendix 2

The two catalysts do not seem to be entirely consistent in structure, as seen below, parts of the high surface catalyst in Figure 29 shows sign of the sheets found the low surface catalyst.



*Figure 29: High surface catalyst with tight sheets*

At the same time regions of the low surface catalyst in shows signs of the less tightly bound sheets. This is seen in Figure 30.



*Figure 30: Low surface catalyst with more relaxed structure*

### Appendix 3 FTIR

For FTIR, a Nicolet IS50 with attached ATR module was used. A DRIFTS cell with a small sample holder was used to obtain results between  $4000\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$ . A background scan was taken using potassium bromide powder before scanning samples. IR results for DRIFTS cell for the ceria powders are seen in Figure 31.

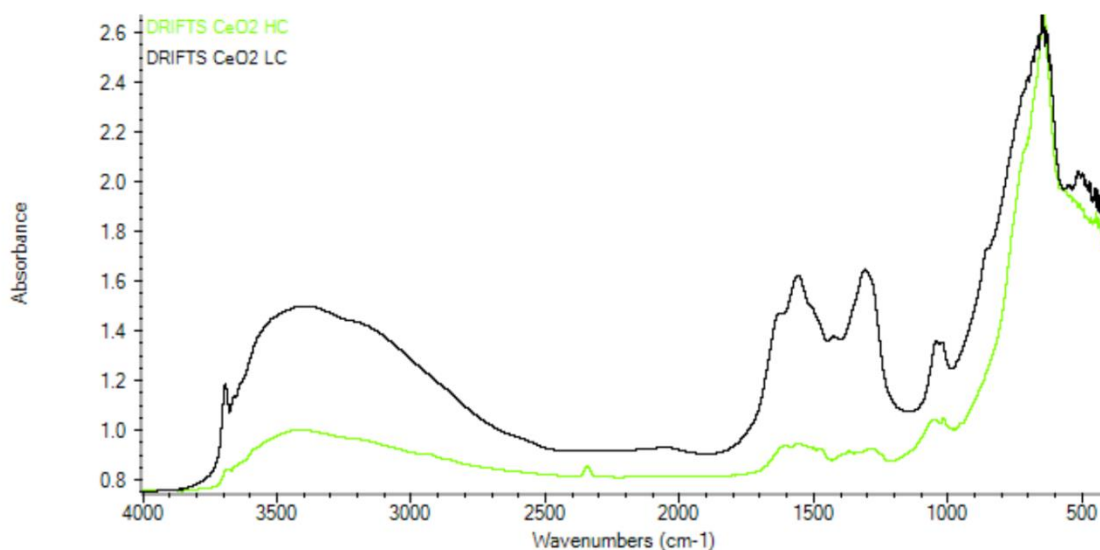


Figure 31: DRIFTS IR results

Result infrared spectroscopy indicated significant differences between the cerium oxide grades, with the high surface cerium oxide showing signs of water contamination peaks between  $1700$  and  $1000\text{ cm}^{-1}$ .



## Appendix 4: XRD scans

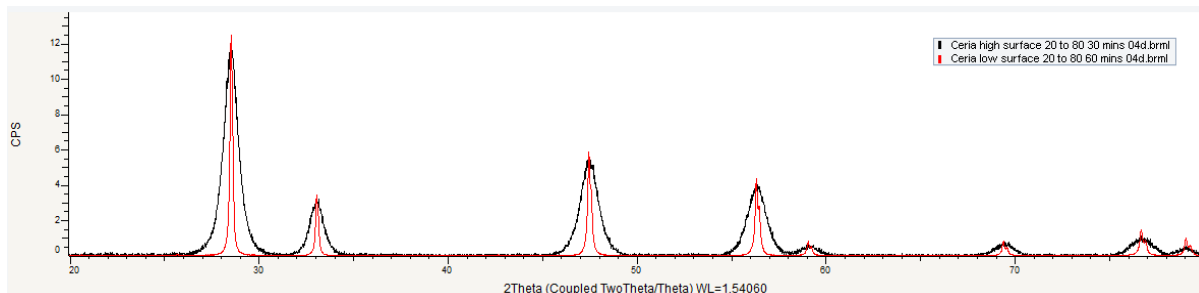


Figure 32: Normalized cerium oxide samples

It can be seen that the low surface cerium oxide is significantly more crystalline, with sharper peaks than the high surface cerium oxide.

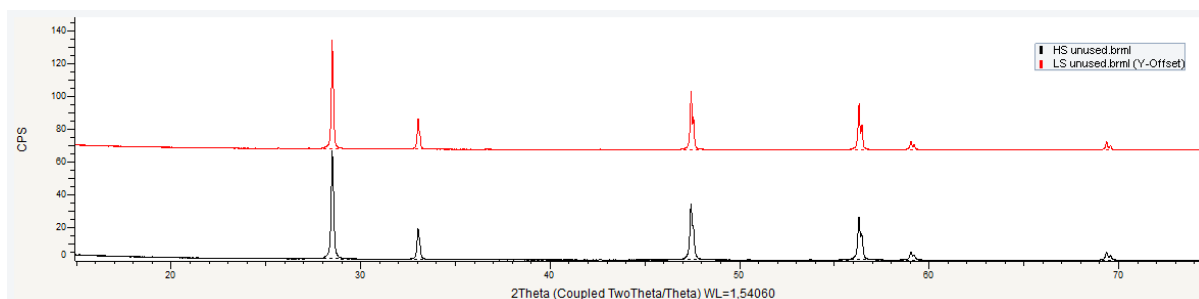


Figure 33: High surface and low surface catalyst

No unexpected phases are present to any visible degree, and the results are fairly similar. On further inspection, the low surface catalyst appears more crystalline, as there is greater peak separation.

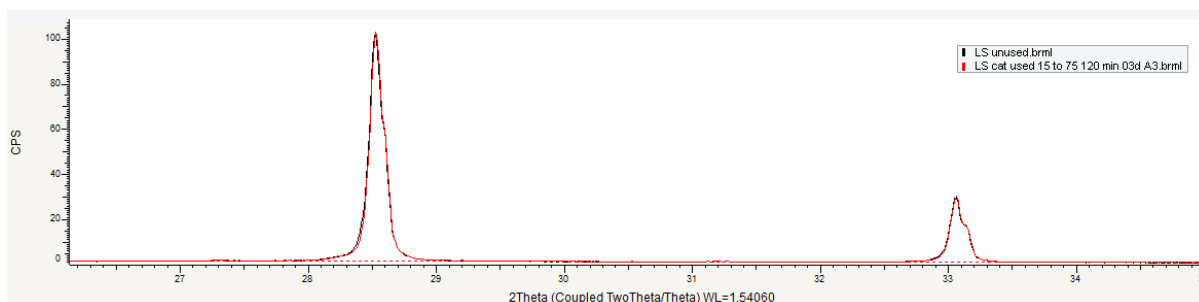


Figure 34: Used an unused low surface catalyst

The difference between used and unused low surface catalyst is negligible.

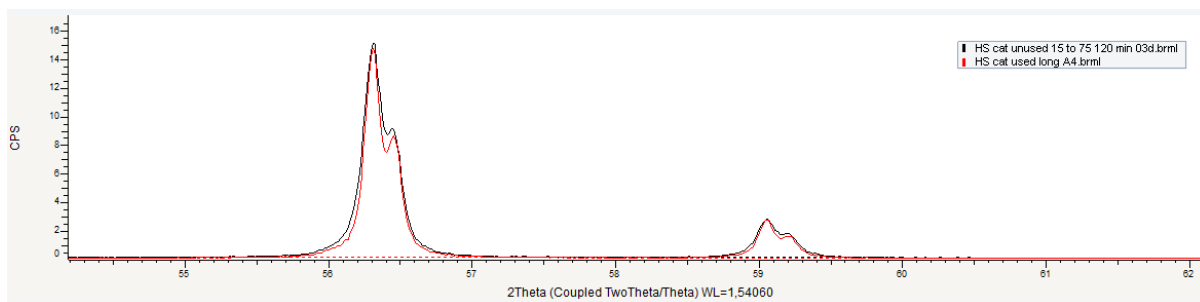


Figure 35: Used and unused high surface catalyst

The used high surface catalyst shows a higher degree of peak separation and thereby a higher crystallinity.