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# Silver catalyst surface changes in structure in various oxygen-containing reactive atmospheres

Master's thesis in Sustainable Chemical and Biochemical Engineering

Supervisor: Hilde Johnsen Venvik

June 2023





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Norwegian University of Science and Technology  
Faculty of Natural Sciences  
Department of Chemical Engineering





# Preface

As a culmination of the master's degree program in Sustainable Chemical and Biochemical Engineering. This master's thesis was created for the Catalysis group at the Department of Chemical Engineering, Norwegian University of Science and Technology.

First, I would like to thank my supervisor, Professor Hilde Johansen Venvik, for excellent guidance and contribution of ideas during the whole research. I would like to thank and express gratitude to Ph.D candidate Youri Van Valen for training and guidance on how to handle and work in the reaction rig and also how to interpret experimental results. I also would like to thank exchange Ph.D Pio Gramazio for help and guidance in data treatment and interpretation. Moreover, I would like to thank the Postdoctoral researcher Tina Bergh for guidance in the interpretation of the results. In addition, a big thank-you to Senior Engineer Estelle Vanhaecke For outstanding guidance and help whenever I needed it.

Finally, I want to thank my family and friends for their never-ending support and for keeping me motivated.

# Declaration of Compliance

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

Trondheim, Norway

A handwritten signature in black ink that reads "Tomasz Skrzydło". The signature is written in a cursive style. Below the signature is a horizontal dotted line.

Tomasz Skrzydło



# Abstract

Formaldehyde can be produced through different routes, with the silver process being one of them. During this process,  $\text{CO}_2$ , CO and  $\text{H}_2$  are being produced from side reactions. Additionally, the surface structure of the silver catalyst is going through a severe change during the process. Based on the points mentioned above the idea of this study was born. The goal of this investigation is to determine and analyse the effect of different atmospheres on the surface structure of silver catalysts. The atmospheres in question are Water vapour, syngas (synthesis gas is a mixture of CO and  $\text{H}_2$ ), CO-water vapour, syngas-water vapour and hydrogen-water vapour mixed with oxygen and nitrogen. The experiments have been set up in the following manner, the silver catalyst of annular configuration was heated up to 650 degrees Celsius in the chosen atmosphere and kept for a specific period. To document the surface evolution during the experimental period Scanning electron microscopy (SEM) was employed. Also, to examine the composition of the silver catalyst Energy dispersive x-ray spectroscopy was performed. The results have shown that each atmosphere investigated had some degree of interaction. The greatest change was observed in syngas-oxygen, syngas-water vapour-oxygen and hydrogen-oxygen-water vapour samples. In the syngas case, big holes and small stepped-like formations were observed. In addition, the activity trend of the reaction was increasing and stabilised at  $\sim 70\%$ , in the case of both CO conversion activity and hydrogen conversion activity. The hydrogen-water vapour-oxygen sample exhibit plateau-like formations on the surface as well as deposition of black material. The activity trend was initially lower than Syngas experiments but then rose and stabilize around 45%. Syngas -water vapour-oxygen sample surface had similarity to traditional MTF surface change. While hydrogen conversion looked similar to the  $\text{H}_2$ - $\text{O}_2$ -water vapour catalytic trend, the CO conversion after the initial rise quickly dropped to 4% activity. The water vapour-oxygen and CO-oxygen-water vapour had a lesser degree on the surface compared to the other samples. In the water vapour-oxygen sample, the triangular pattern appearing on the surface was observed. CO-oxygen-water vapour also showed a triangular pattern on the surface, but also white spots appeared on the surface. Similarly, the CO conversion is syngas- $\text{O}_2$ -water vapour after the initial rise the conversion quickly dropped to 1% level.



# Sammendrag

Formaldehyd kan produseres gjennom forskjellige ruter, med sølvprosessen som en av dem. Under denne prosessen produseres CO<sub>2</sub>, CO og H<sub>2</sub> fra bireaksjoner. I tillegg gjennomgår overflatestrukturen til sølvkatalysatoren en alvorlig endring i løpet av prosessen. Basert på punktene nevnt ovenfor ble ideen om denne studien født. Målet med denne undersøkelsen er å bestemme og analysere effekten av forskjellige atmosfærer på overflatestrukturen til sølvkatalysatorer. Atmosfærene det er snakk om er Vanndamp, Syntesegass (syntesegass er en blanding av CO og H<sub>2</sub>), CO-vanndamp, Syngass-vanndamp og hydrogen-vanndamp blandet med oksygen og nitrogen. Eksperimentene er satt opp på følgende måte, sølvkatalysatoren med ringformet konfigurasjon ble varmet opp til 650 grader Celsius i den valgte atmosfæren og holdt i en bestemt periode. For å dokumentere overflateutviklingen i løpet av forsøksperioden ble skanneelektronmikroskopi (SEM) brukt. Energidispersiv røntgenspektroskopi ble også utført for å undersøke sammensetningen av sølvkatalysatoren. Resultatene har vist at hver atmosfære som ble undersøkt hadde en viss grad av interaksjon. Den største endringen ble observert i syngass-oksygen, syngass-vanndamp-oksygen og hydrogen-oksygen-vanndampprøver. I syngas-tilfellet ble det observert store hull og små trinnlignende formasjoner. I tillegg økte aktivitetstrenden til reaksjonen og stabiliserte seg ved ~70 %, i tilfelle av både CO-omdannelsesaktivitet og hydrogenomdannelsesaktivitet. Hydrogen-vanndamp-oksygenprøven viser platåliggende formasjoner på overflaten samt avsetning av svart materiale. Aktivitetstrenden var i utgangspunktet lavere enn Syngas-eksperimenter, men steg deretter og stabiliserte seg rundt 45 %. Syngas-vanndamp-oksygen prøveoverflate hadde likhet med tradisjonell MTF overflateendring. Mens hydrogenkonvertering så ut som den katalytiske H<sub>2</sub>-O<sub>2</sub>-vanndamp-trenden, falt CO-konverteringen etter den første økningen raskt til 4 % aktivitet. Vanndamp-oksygen og CO-oksygen-vanndamp hadde en mindre grad på overflaten sammenlignet med de andre prøvene. I vanndamp-oksygenprøven ble det trekantede mønsteret som vises på overflaten observert. CO-oksygen-vanndamp viste også et trekantede mønster på overflaten, men også hvite flekker oppstod på overflaten. På samme måte som CO-omdannelsen er syngass-O<sub>2</sub>-vanndamp etter første stigning, og omdannelsen falt raskt til 1 % nivå.





# Table of Contents

Preface.....	v
Abstract .....	vii
Sammendrag .....	ix
Table of Contents .....	xi
Abbreviations.....	xiii
List of symbols .....	xiv
List of Figures .....	xv
List of Tables .....	xvii
Chapter 1 Introduction .....	1
1.1 Motivation .....	1
1.2 Goal .....	1
1.3 Project organisation .....	1
Chapter 2 Theory .....	3
2.1 Silver process.....	3
2.2 Mixed oxide process .....	4
2.3 The silver-oxygen interaction .....	5
2.4 Catalyst characterization.....	6
2.4.1 Scanning Electron Microscopy .....	6
2.4.2 Energy-Dispersive X-ray spectroscopy .....	7
2.5 Gas chromatography .....	8
2.6 Annular catalyst concept.....	8
Chapter 3 Experimental.....	11
3.1 Risk assessment .....	11
3.2 Experimental Setup.....	11
3.3 Catalyst preparation .....	12
3.4 Specialization project overview .....	13
3.5 Methodology .....	14
Chapter 4 Results and discussion.....	17
4.1 Water experiment results.....	17
4.1.1 SEM results .....	17
4.1.2 EDX results .....	19
4.2 Syngas results.....	21
4.2.1 SEM images.....	21
4.2.2 EDX images.....	23
4.2.3 Activity .....	24
4.3 CO-water oxidation results .....	25
4.3.1 SEM results .....	25

4.3.2 EDX results .....	27
4.3.3 Activity .....	28
4.4 Hydrogen and water experiments.....	29
4.4.1 SEM results .....	29
4.4.2 EDX results .....	31
4.4.3 Activity .....	32
4.5 Syngas and water experiments .....	33
4.5.1 SEM results .....	33
4.5.2 EDX results .....	35
4.5.3 Activity .....	36
4.6 Discussion.....	37
4.6.1 Temperature effect discussion .....	37
4.6.2 CO experiments overview.....	37
4.6.3 Hydrogen experiments overview .....	39
Chapter 5 Conclusion and future work.....	41
5.1 Conclusion .....	41
5.2 Future work .....	42
Bibliography.....	43
Appendix A – Water-oxygen experiments .....	I
Appendix B – Syngas oxidation experiments .....	IX
Appendix C – CO oxidation with water vapour experiment .....	XVII
Appendix D – Hydrogen oxidation with water vapour experiment.....	XXV
Appendix E – Syngas Oxidation with water vapour experiment.....	XXXIII
Appendix F – Risk Assessment .....	XLI
Appendix G – Elemental analysis of silver .....	XLII

# Abbreviations

## Abbreviation Definition

CEM	Controlled Evaporator and Mixer
CH <sub>2</sub> O	Formaldehyde
CH <sub>3</sub> OH	Methanol
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
EDX	Energy Dispersive X-ray Spectroscopy
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
MFC	Mass-flow controller
MTF	Methanol to Formaldehyde
O <sub>2</sub>	Oxygen
SEM	Scanning electron Microscopy
Syngas	Synthesis gas

# List of symbols

$\Delta H$	Heat of the reaction
$O_\alpha$	Oxygen alpha
$O_\beta$	Oxygen beta
$O_\gamma$	Oxygen gamma
$T_{bed}$	Bed temperature
$T_{max}$	Maximal temperature
$T_{set}$	Setpoint temperature
$p_{CO}$	Partial pressure of CO

# List of Figures

<b>Figure 2.1</b> General schematic of the silver process formaldehyde plat .....	4
<b>Figure 2.2</b> General schematic of Formox process .....	5
<b>Figure 2.3</b> General scheme of interaction of chemisorbed species of oxygen .....	6
<b>Figure 2.4</b> General schematic of Scanning Electron Microscope .....	7
<b>Figure 2.5</b> General schematic of the EDS setup .....	8
<b>Figure 2.6</b> General schematic of the annular reactor .....	9
<b>Figure 3.1</b> General schematic of the rig.....	12
<b>Figure 3.2</b> General view of the scratch on the catalyst .....	12
<b>Figure 3.3</b> General overview of area selection for investigation .....	13
<b>Figure 3.4</b> The changes observed in the catalyst subjected to A - H <sub>2</sub> -O <sub>2</sub> atmosphere after 84h experiment; B - synthetic air atmosphere after 84h experiment; C - CO-O <sub>2</sub> atmosphere after 84h experiment and D - N <sub>2</sub> atmosphere after 84h experiment. ....	14
<b>Figure 3.5</b> Graph showing catalyst evolution where A – 12h and B- 36h.....	14
<b>Figure 3.6</b> Graph showing temperature profiles of experiments.....	16
<b>Figure 4.1</b> Image of triangular pattern present on the surface .....	17
<b>Figure 4.2</b> Surface evolution of the silver catalyst under water vapour containing atmosphere. Where A, B – fresh; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. (T <sub>bed</sub> = ~620°C) .....	18
<b>Figure 4.3</b> The results of EDX analysis of the catalyst under water vapour - oxygen atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.....	19
<b>Figure 4.4</b> Surface evolution if silver catalyst under syngas-oxygen atmosphere. Where A, B – fresh catalyst; C, D – after 12h; E, F – after 36h; G, H – after 84h. (T <sub>bed</sub> = ~620°C) .....	22
<b>Figure 4.5</b> The results of EDX analysis of the catalyst under syngas- oxygen atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.....	23
<b>Figure 4.6</b> Comparative graphs showing the conversion of both CO (A) and Hydrogen (B) during the experimentation period. (T <sub>bed</sub> = ~620°C).....	24
<b>Figure 4.7</b> The white spots present in the catalyst subjected to CO – water vapour atmosphere. (T <sub>bed</sub> = ~620°C, 84h experiment) .....	25
<b>Figure 4.8</b> Surface evolution if silver catalyst under CO-water vapour-oxygen atmosphere. Where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. (T <sub>bed</sub> = ~620°C) .....	26
<b>Figure 4.9</b> The results of EDX analysis of the catalyst under CO-oxygen-water vapour atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.....	27
<b>Figure 4.10</b> Graph showing conversion of CO during investigation period. (T <sub>bed</sub> = ~620°C) .....	28
<b>Figure 4.11</b> The zoomed in area of the graph of CO conversion during CO-water oxidation .....	28
<b>Figure 4.12</b> The growth of the black matter on the catalyst surface. Where A - after 36h and B - after 84h.....	29
<b>Figure 4.13</b> Evolution of the catalyst surface under Hydrogen-oxygen-water vapour atmosphere where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. (T <sub>bed</sub> = ~620°C) .....	30
<b>Figure 4.14</b> The results of EDX analysis of the catalyst under hydrogen – water vapour - oxygen atmosphere after 84h experiment. Where A – image oh investigated area with markings of the spectra, B – graph showing off spectra obtained.....	31
<b>Figure 4.15</b> Conversion graphs for the Hydrogen oxidation in the presence of water vapour. (T <sub>bed</sub> = ~620°C).....	32

<b>Figure 4.16</b> The small crystals present on the surface of the catalyst.....	33
<b>Figure 4.17</b> Evolution of the catalyst surface under Syngas-oxygen-water vapour atmosphere where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. ( $T_{bed} = \sim 620^{\circ}\text{C}$ ) .....	34
<b>Figure 4.18</b> The results of EDX analysis of the catalyst under syngas – water vapour - oxygen atmosphere after 84h experiment. Where A – image oh investigated area with markings of the spectra, B – graph showing off spectra obtained.....	35
<b>Figure 4.19</b> Conversion graphs for the Syngas oxidation in the presence of water vapour. Where A is CO conversion during experimental period and B Hydrogen conversion during experiments. ( $T_{bed} = \sim 620^{\circ}\text{C}$ ).....	36
<b>Figure 4.20</b> Comparison of CO experiment depending on the mixture. Where A – 12h experiment, B – 36h experiments and C – 84h experiments. ....	38
<b>Figure 4.21</b> Comparison of hydrogen experiment depending on the mixture. Where A – 12h experiment, B – 36h experiments and C – 84h experiments.	39

# List of Tables

**Table 3. 1** Conditions for the experimental series .....15





# Chapter 1 Introduction

## 1.1 Motivation

Formaldehyde is an organic compound from the aldehyde group having a chemical formula of  $\text{CH}_2\text{O}$ , mostly produced from methanol in industrial production[1]. Its main application is to be a precursor to various polymer compounds such as urea-formaldehyde resin, melamine resin and polyoxymethylene plastics[1-4]. These resins can be used in construction, synthetic fabric production, and the furniture industry [5]. Additionally, ~40% formaldehyde dissolved in water called formalin is used as a preservative agent to preserve tissue samples.

Industrially there are 2 main routes for formaldehyde production. The silver-catalysed process employs electrolytic pure silver and runs in air-lean conditions with steam. The second route uses metal oxides typically iron with molybdenum or vanadium, in excess air [6]. The demand for formaldehyde has been increasing and is expected to rise further. This makes research into maximizing yield interesting [5]. There were many investigations conducted to tackle the possibility of optimization of the production of formaldehyde. Research is also currently being done in finding a new catalyst for the process [7]. Another area that the investigation conducted was the optimization of energy consumed by this process.

## 1.2 Goal

This investigation aims to determine the effect of the compounds that can be observed produced or/and put with feed to the formaldehyde reaction on the silver catalyst as well as the degree of any interaction that may occur. Additionally, the goal of this study is to link the structural changes to the activity in oxidation reactions. To observe the physical changes done to the catalyst Scanning electron microscopy was employed to record the possible evolution of the surface and an Energy dispersive x-ray characterization technique was employed to check the composition of the catalyst during and after the experiment period as well as analyse any potential anomaly present on the surface.

## 1.3 Project organisation

The master's thesis is a continuation of a specialization project completed in autumn 2022 but with new reaction atmospheres. There have been lots of investigations conducted analysing the Methanol-to-Formaldehyde (MTF) reaction, but few have focused on the effect of side reaction products on the reaction surface.

With the guidance of master supervisors and the help of PhD students, the scientific work schedule as well as appropriate characterization techniques were chosen.

The theoretical background of the thesis was created, based on exploring various scientific databases by searching for relevant topics. The literature surrounding the effect of side reaction products on the reaction surface, in a given temperature range on pure silver catalyst, was limited.

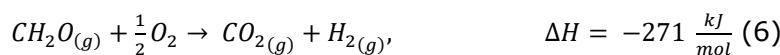
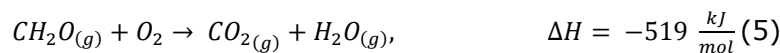
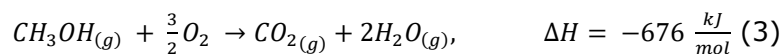
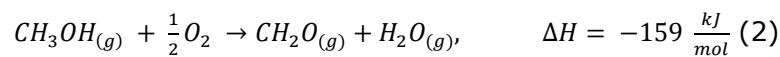
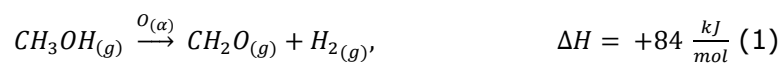
This thesis is part of the iCSI Industrial Innovative Area 3 on Frontier Formalin Development.



# Chapter 2 Theory

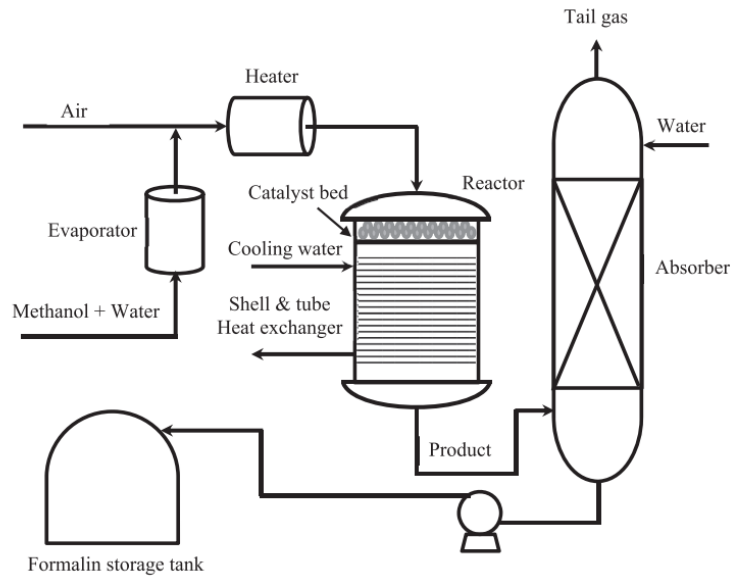
## 2.1 Silver process

The BASF process, also known as the silver process, employs pure silver as a catalyst for dehydrogenation and partial oxidation of methanol to formaldehyde [7]. The reaction takes place at  $\sim 600^\circ\text{C}$  with a methanol-rich mixture. A mixture of methanol and, is evaporated and mixed with air. The gas mixture is passed through a fixed bed reactor with silver granules. The product mixture is rapidly quenched to prevent side reactions as formaldehyde is highly reactive. In the next step, the product gas is directed into the adsorption column where formaldehyde is being separated. The unreacted methanol is also being separated, recycled, and passed again with another run. The product from this process is a solution of formaldehyde in water [7]. The generalized reaction scheme is shown below.



As it can be seen from the reaction equations above the main side-product of this process are carbon dioxide and its formation represents a loss of formaldehyde. The pathway of  $\text{CO}_2$  is not fully understood, while  $\text{CO}$  is likely to form via (7) homogeneously.  $\text{H}_2$  also forms from (1). Additionally,  $\text{CO}$  and  $\text{H}_2$  can undergo the gas phase reaction with other components of the mixture.

The single-pass conversion of methanol to formaldehyde is around 65-75%. Unconverted methanol is recycled to decrease the consumption of fresh methanol. The overall yield of the silver process is 90% and the lifetime of the silver catalyst is several months at the industrial plant. Figure 2.1 shows a typical arrangement of the silver process set up at an industrial plant [8].

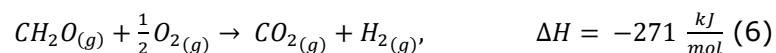
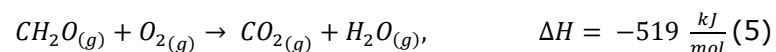
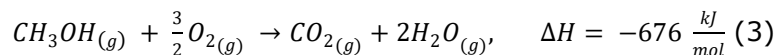
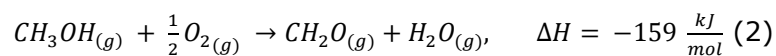


**Figure 2.1** General schematic of the silver process formaldehyde plant [8]

The silver process mode of operation gives some advantages. One of the advantages of using silver is the ability to lower the cost of buying new catalysts, due to the regeneration of silver. Additionally, the use of excess methanol allows the reduction of reactor and utilities [8].

## 2.2 Mixed oxide process

Another process that produces formaldehyde is called the mixed oxide process since the catalyst employed is the mixed oxide of iron, molybdenum and sometimes vanadium. The Formox process uses the said mixed oxide catalyst [9]. The process takes place in an excess air atmosphere at a lower temperature than the silver process, which reduces the risk of explosion during the process but has a higher risk in the startup phase of the process. Additionally, the operation in excess air ensures full conversion of methanol. The general reaction scheme for the reaction is shown below[10].

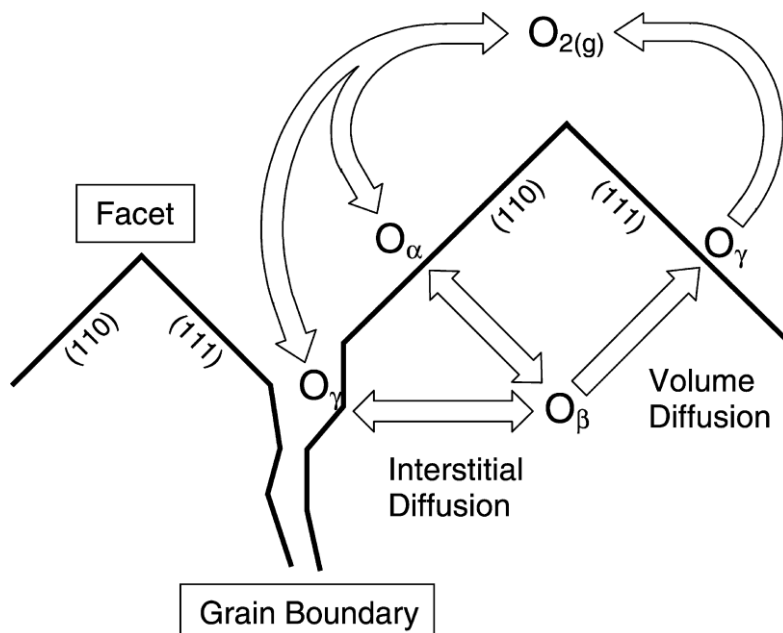


The temperature range in that the reaction takes place is below 400°C with the typical yield of the reaction is 95% and 98-99% conversion with the average lifetime of the catalyst is between 6 to 12 months. The general scheme of the mixed oxide process is shown in figure 2.2. The concept of the process was originally designed by Perstorp and Reichhold Chemicals now owned by Johnson Matthey [9].



$O_\gamma$  is bound stronger to silver surface than  $O_\alpha$  but not as strongly incorporated into the lattice of silver as  $O_\beta$ . It is formed due to volume diffusion of  $O_\beta$  through (111)-terminated lattice. The research indicates that the  $O_\gamma$  is responsible for catalysing the reaction of methanol to formaldehyde [13,14].

Figure below represents the general scheme of interaction of distinct species of chemisorbed oxygen.

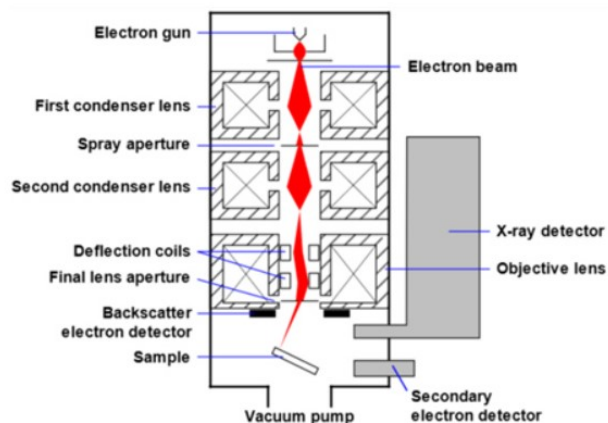


**Figure 2.3** General scheme of interaction of chemisorbed species of oxygen [13]

## 2.4 Catalyst characterization

### 2.4.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to observe changes to the catalyst surface. The technique uses a focused electron beam that scans the surface and produces signals that are then captured by detectors and translated into images. The signals produced during the SEM can be characterized as secondary electrons, back-scattered electrons, and characteristic x-rays [15, 19]. The figure below shows the general scheme of the Scanning electron microscope.



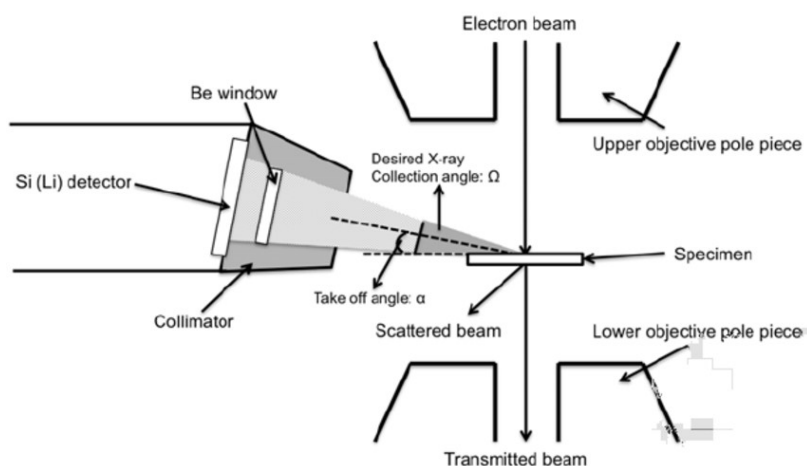
**Figure 2.4** General schematic of Scanning Electron Microscope [16]

Secondary electrons are produced during the bombardment of the material surface due to its ionization. Secondary electrons have small energy around 50 eV. Due to this low energy, they are only observed when they originate at or a few nanometres below the surface. This makes it a useful instrument to gather information about the topography of the catalyst [17].

Back-scattered electrons are created by the reflection of them from the surface. The literature states that the electrons created this way have much higher energy. They can be generated from much deeper layers of sample substance than secondary electrons [18].

#### 2.4.2 Energy-Dispersive X-ray spectroscopy

Energy-Dispersive X-ray spectroscopy (EDX) is a characterization technique that allows for the analysis of the elemental composition of given sample material by creating specific energy x-rays with an electron beam [19, 21]. The x-rays are created by exciting the ground state valence shell electrons. When these electrons return to the ground state, they emit x-rays with a specific energy. When detected x-rays are translated into peaks giving the information about the identity of the element as well as the amount [19, 20, 21]. The fig. 2.5 shows the general schematic of the EDS setup.



**Figure 2.5** General schematic of the EDS setup [21]

## 2.5 Gas chromatography

Gas chromatography (GC) is a technique that allows to analyse semi-volatile and volatile compounds [22]. The sample gas is led through the column containing stationary phase. The sample is carried by a carrier gas. In principle, the GC can separate the compounds of the mobile phase based on the size of the particles and/or compounds and their boiling point. The separation is achieved by slowing the movement of some of the components of the gas mixture [22]. Additionally, the separation can be achieved also with use of the stationary phase present in the column. After calibration of the GC, we can quantify the amount of gasses present in the sample gas mixture [22].

The mobile phase or carrier gas in gas chromatography is a substance that carries sample material through the column. The mobile phase must be inert or in other words not reactive to the sample material or stationary phase in the chromatograph column. Typical gases used for the mobile phase of gas chromatograph are helium, argon, nitrogen, or hydrogen [22].

The stationary phase in the gas chromatograph is located at the column and it is usually viscous liquid or solid. The properties of the stationary phase are depended on the character of the sample due to there are columns specifically made to separate polar, nonpolar, hydrophilic and/or hydrophobic compounds [22].

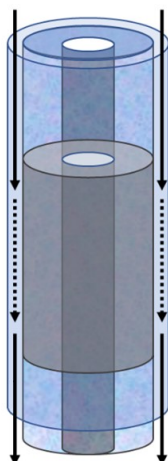
## 2.6 Annular catalyst concept

There are several industrially relevant products that are obtained from the partial oxidation pathway. But when the complete oxidation occurs in these processes, it results in creation of unwanted by-products such as carbon dioxide. The situation mentioned can be applied to the MTF process. From the need to limit the full oxidation of the mixture short contact time reactors were employed. Due to achieving the contact time from 100ms to 1ms, they limit the possibility of side reaction due to optimal temperature control [23]. Additionally, they provide good mixing and uniform residence time on the catalyst, which leads to low selectivity, suppression of heterogeneous gas phase, minimized flames and explosion and



achieving higher yields and selectivities [23]. One of the types of short contact time reactor is annular reactor.

An annular reactor is constructed in the following manner, the thin layer of catalyst is being coaxially inserted into an outer quartz tube with narrow channel openings [24, 25]. This set up allows for the creation of a laminar flow regime. Additionally, the design of the reactor allows to reduce the importance of the mass transfer limitations, allows operation outside of the equilibrium conditions and it also creates almost isothermal conditions inside the reactor. The scheme of the annular reactor used in investigation can be seen in the figure below.



**Figure 2.6** Schematic of the annular reactor used in investigation [35].

The properties of the reactor mentioned above made the reactor suitable for kinetic investigation of some processes such as methane partial oxidation [25, 26], light paraffins oxidative dehydrogenation [27] as well as the MTF process [28].



# Chapter 3 Experimental

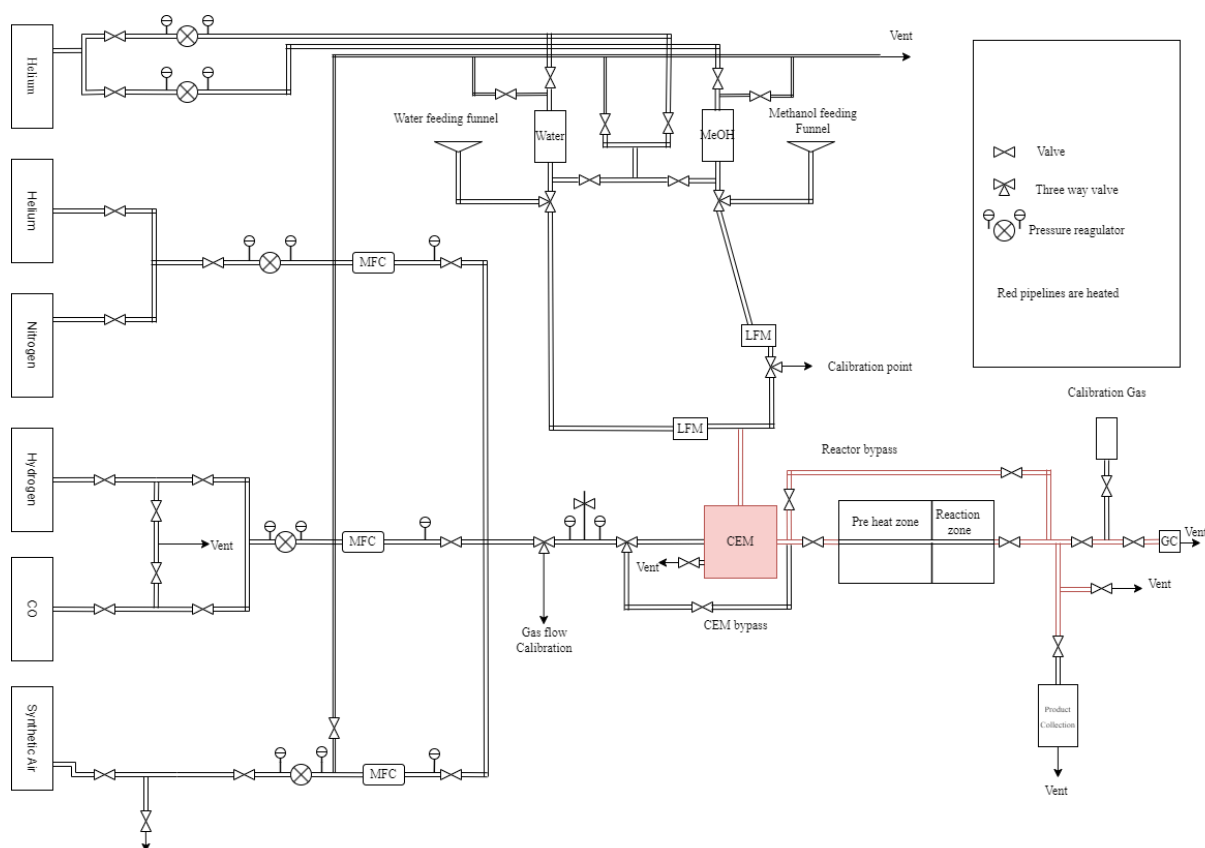
## 3.1 Risk assessment

To ensure that the experiments were conducted safely and pose no danger to the experimentalist and other people and personnel, a risk assessment was performed. The NTNU Risk assessment protocol's ID-number 51097 has a schematic entry for safety precautions and risks related to this study. Appendix F contains an overview of the risk assessment. Additionally, the Norwegian University of Science and Technology's after-hours agreement was approved and adhered to.

The use of combustible gasses posed the greatest risk during this work. Hydrogen (explosive) and carbon monoxide (toxic) were regularly used. Measures were taken to mitigate the chance using aforementioned gasses. The experiments took place in an enclosed rig with a ventilation system and an array of gas detectors. The rig was leak tested before each series of experiments.

## 3.2 Experimental Setup

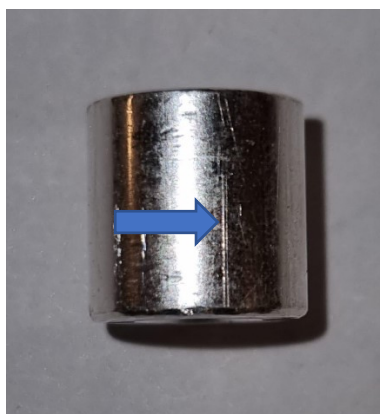
The experiments were conducted at rig 1.3 at NTNU. The flow diagram is shown in figure 3.1. Gas flows are controlled using Bronkhorst mass-flow controllers (MFC) that were calibrated for the following gases: nitrogen, synthetic air, syngas, carbon monoxide, and hydrogen. A Bronkhorst Controlled Evaporator and Mixer (CEM) was used to feed water and mix this with the gas stream. The Gas stream enters a quartz reactor situated in a 2-zone furnace, a pre-heating zone (top,  $T_{\max} = 200^{\circ}\text{C}$ ) and a reaction zone (bottom,  $T_{\max} = 700^{\circ}\text{C}$ ). The catalyst is placed in the reaction zone. They are both programmed and controlled with Eurotherm temperature controllers. The MFCs can be controlled using the LabView software on a nearby computer. Nitrogen, Air, and the reactant gas have separate MFC each. To switch between CO, H<sub>2</sub>, and Syngas different gas cylinders were used. The temperature program was pre-programmed using iTools Engineering software and then manually activated on the Eurotherm temperature controllers. The set up also allows us to swap between two different modes of operation, that is the flow of gases alone and gases with water which is directed to the CEM. The set up also allows to switch between the line that leads to the reactor that later leads to the gas chromatographer and the line that is bypassing it to reach the gas chromatographer. A schematic overview of the experimental setup is shown in Figure 3.1.



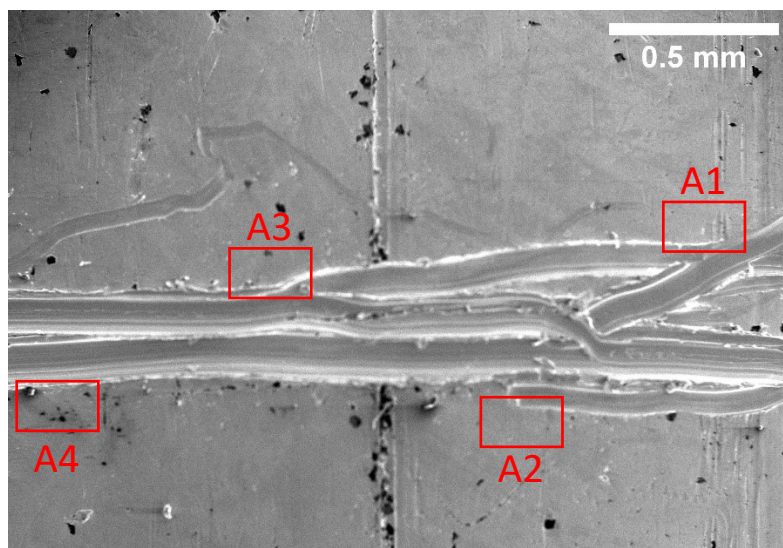
**Figure 3.1** General schematic of the rig

### 3.3 Catalyst preparation

The silver rod was bought from Goodfellow™. The rod was cut to cylinders 1cm in length and an outside diameter of 10 mm, to create annular bulk silver catalyst. The next step was to scratch the surface as shown by the arrow in figure 8. This was done to create a reference point to help identify the selected areas on the catalyst surface as it is shown in figures 3.2 and 3.3. Appendix G contains the elemental analysis of the fresh catalysts.



**Figure 3.2** General view of the scratch on the catalyst



**Figure 3.3** General overview of area selection for investigation

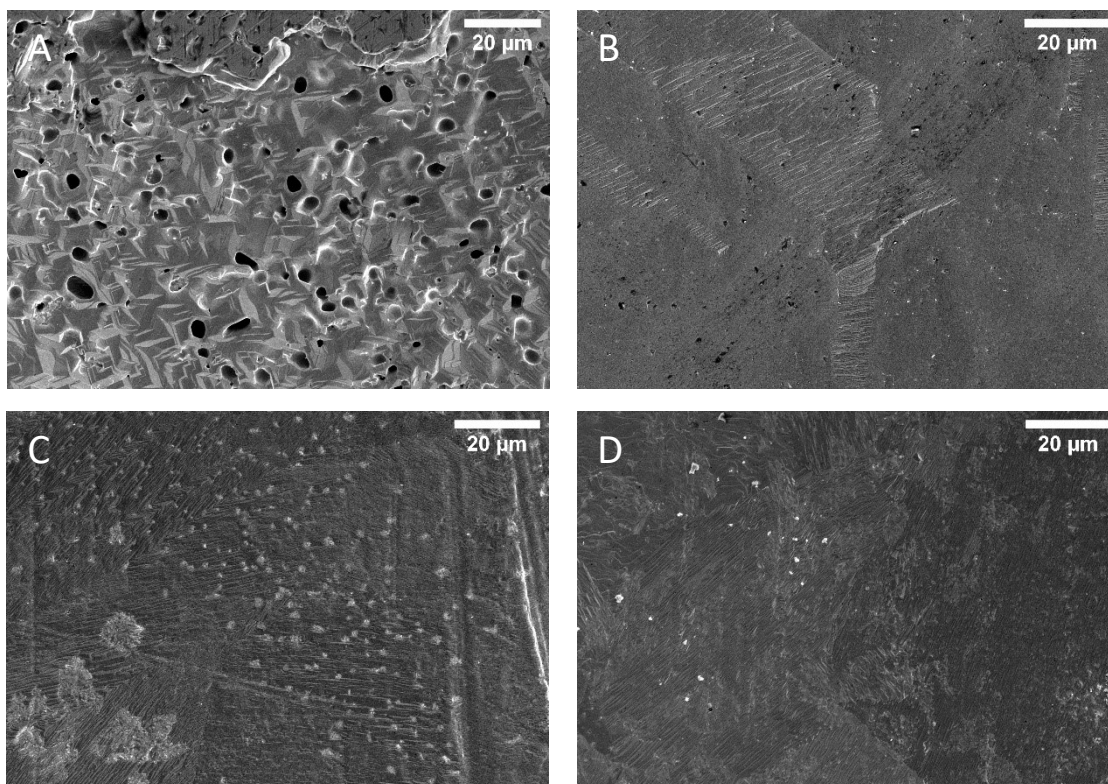
### 3.4 Specialization project overview

The specialization project was conducted in the autumn of 2022. The goal of that project was to investigate structural changes and chemical interaction of the silver catalyst in different atmospheres. The atmospheres chosen for that study were CO-oxygen, H<sub>2</sub>-oxygen, Nitrogen atmosphere (99,999%) and synthetic air (N<sub>2</sub> 79%, O<sub>2</sub> 21%) [29]. The experiments were set up in following manner: the fresh annular silver catalyst was placed into the reactor. Then the flow was started with a total flow of 125 Nml/min. In next step the temperature program was started with  $T_{\text{set}} = 650^{\circ}\text{C}$  and 3 separate cycles were performed namely 12h, 36h, and 84h [29].

The catalyst subjected to the hydrogen-oxygen atmosphere had the greatest surface change in the experimental series. The main surface modifications were big holes dotting the surface as seen in figure 3.3 A.

A medium degree of changes were observed in catalysts subjected to the synthetic air atmosphere and CO-oxygen atmosphere. In a synthetic air atmosphere, the surface became more flattened than before the experimental period and its surface was dotted with pinholes as seen in figure 3.3 B. The CO-oxygen atmosphere enforced more stepped-like structure on the catalyst as well as more facets formation as shown in figure 3.3 C.

In the case of nitrogen atmosphere, the surface experienced the smallest number of changes compared to the previously selected atmospheres. A small amount of triangular pattern was observed on the surface of the catalyst. Additionally, some grain formation was observed in addition to a small amount of pinholes forming that can be observed in figure 3.3 D.

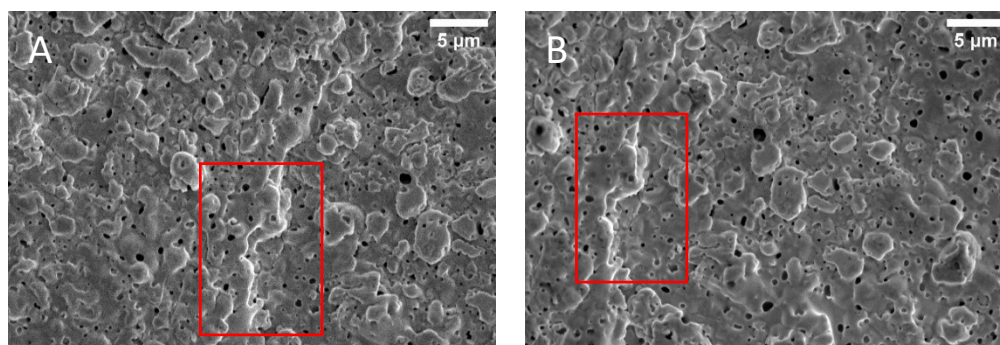


**Figure 3.4** The changes observed in the catalyst subjected to A -  $\text{H}_2\text{-O}_2$  atmosphere after 84h experiment; B - synthetic air atmosphere after 84h experiment; C -  $\text{CO-O}_2$  atmosphere after 84h experiment and D -  $\text{N}_2$  atmosphere after 84h experiment.

### 3.5 Methodology

To begin the experiment the flow was stabilized on the bypass line for a few hours. The gas composition was tracked using the GC. When the flow was deemed stable, the catalyst was inserted into the reactor. If the experiment was conducted with water vapour present, then the reactor was also pre-heated to  $100^\circ\text{C}$  to avoid condensation. The next step was to swap the flow from the bypass line to the reactor line. After the flow has stabilized on the reactor line the experiments were started.

The conditions and atmospheres investigated can be found in table 3.1. A fresh catalyst was used for each reaction condition. Each catalyst was exposed to the reaction conditions for three cycles: 12, 36, and 84 hours. These Cycles can be seen in figure 3.5 and are the same as in [29]. After each cycle, the surface was inspected using SEM and EDX.

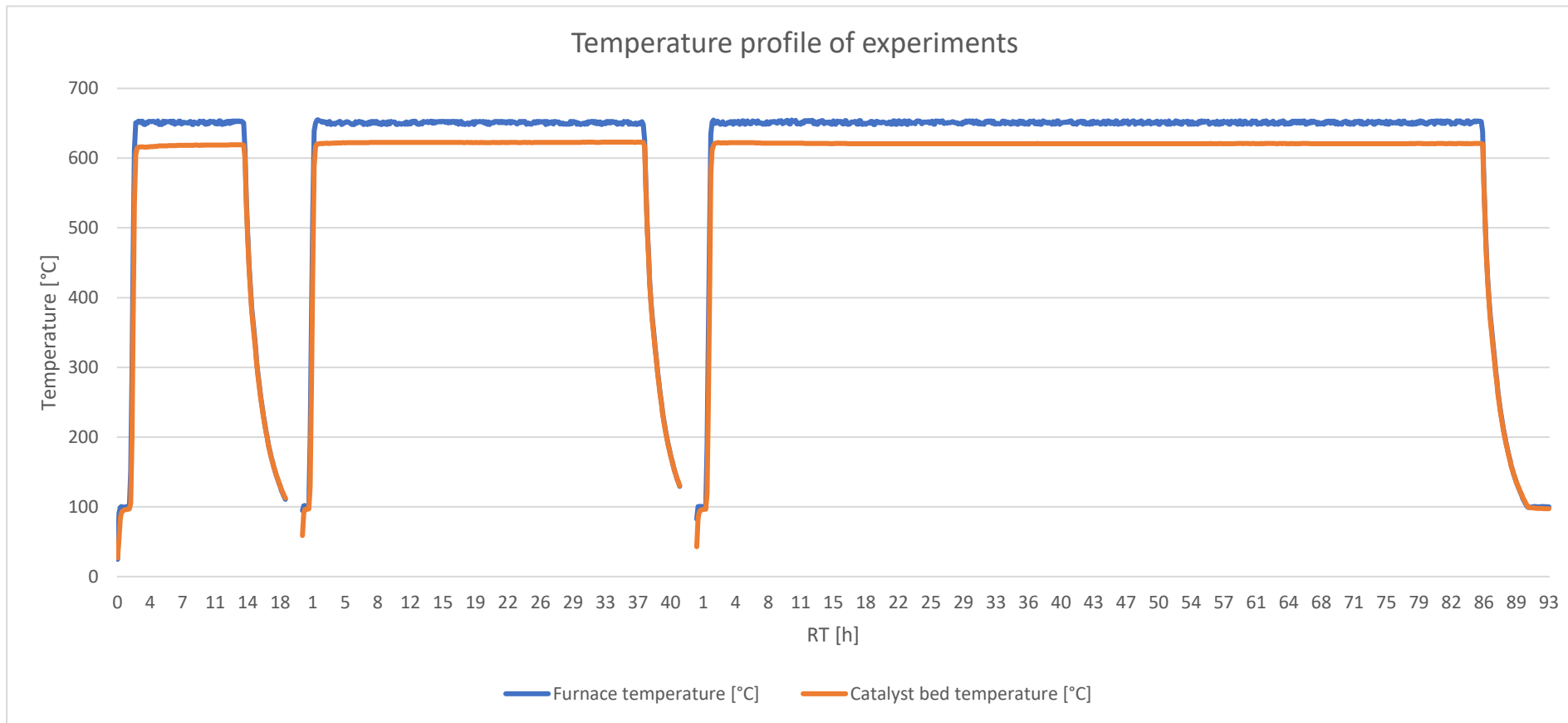


**Figure 3.5** Graph showing catalyst evolution where A – 12h and B- 36h.

Recognizable features as shown in figure 3.4 and highlighted by red rectangles, helped in the determination of the chosen spot. By finding those features on the surface, it allowed the experimenter to be sure that the image was taken of the same area on the sample after each cycle step.

<b>Experiment name</b>	<b>Temperature</b>	<b>Total gas flow</b>	<b>Composition</b>
Water-oxygen	650°C furnace temperature	125 Nml/min	H <sub>2</sub> O 11 mol% O <sub>2</sub> 6 mol% N <sub>2</sub> 81 mol%
Syngas oxidation	650°C furnace temperature	125 Nml/min	CO 2 mol% H <sub>2</sub> 2 mol% O <sub>2</sub> 6 mol% N <sub>2</sub> 90 mol%
Syngas oxidation with water	650°C furnace temperature	125 Nml/min	CO 2 mol% H <sub>2</sub> 2 mol% O <sub>2</sub> 6 mol% H <sub>2</sub> O 11 mol% N <sub>2</sub> 79 mol%
CO oxidation with water	650°C furnace temperature	125 Nml/min	H <sub>2</sub> O 11 mol% CO 2 mol% O <sub>2</sub> 6 mol% N <sub>2</sub> 81 mol%
Hydrogen oxidation with water	650°C furnace temperature	125 Nml/min	H <sub>2</sub> O 11 mol% H <sub>2</sub> 2 mol% O <sub>2</sub> 6 mol% N <sub>2</sub> 81 mol%

**Table 3.1** Conditions for the experimental series



**Figure 3.6** Graph showing temperature profiles of experiments.



# Chapter 4 Results and discussion

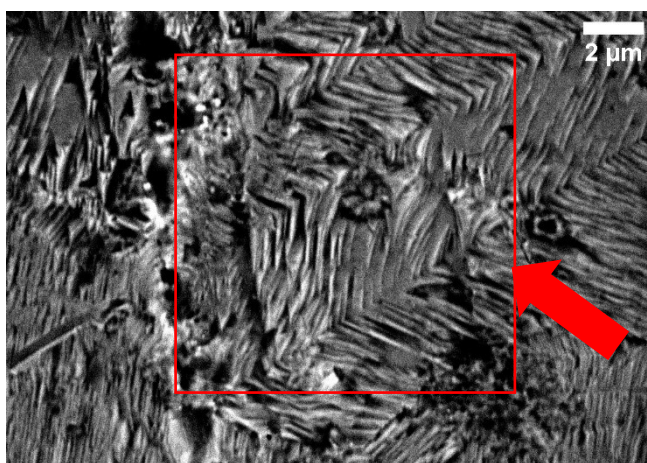
## 4.1 Water experiment results

The idea to investigate the water effect on the surface of silver catalyst came from the setup of the MTF silver process. In said process, the water is added to the feed of the process to control bed temperature. Additionally, the addition of water has increased both conversion of the process and selectivity towards formaldehyde [28]. So, it was beneficial to investigate water vapour interaction with the silver surface in presence of oxygen.

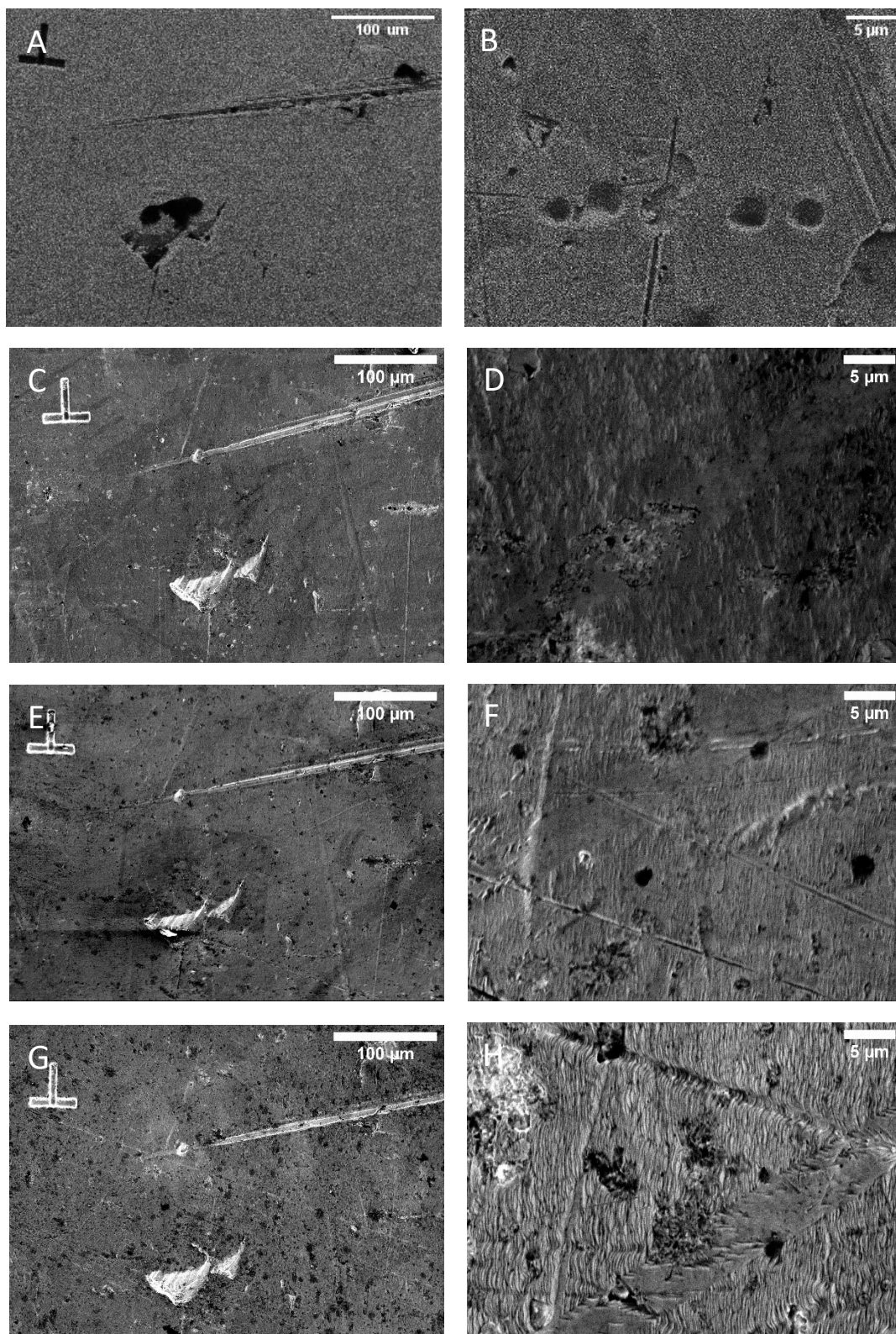
### 4.1.1 SEM results

The surface evolution shown in the figure 4.2. As it can be observed the surface have undergone minor changes during experimental period. There is visible effect on the surface such as a triangular pattern on the surface of the catalyst as it is shown by red rectangle in figure 4.1. This triangular pattern present of the surface seems to be aligned with the orientation of the grain. As mentioned, similar pattern of surface change was observed in experiment conducted with use of nitrogen on the catalyst surface. From this we can see that water in presence of oxygen act like the inert or partially inert due to higher restructuring of the surface but having still recognizable areas present.

Similar observations were made during the nitrogen exposure experiments in the specialization project [29] as well as observed by Millar et al. [30]. But it must be noted that Millar have used  $\text{Ag}_2\text{O}$ , that he reduced to pure silver and not bulk silver catalyst at slightly different conditions which will have the impact on the overall interaction of silver catalyst. The surface structure after 84h can be still recognized even though there are signs of restructuring of surface, but the degree of reconstruction was smaller than the those observed during exposures to the more reactive gasses reconstruction of the surface. Since the experiments were conducted above Tammann temperature [31] it was expected that some surface change would occur. Given the previous specialization [29] project and literature [30, 31, 32, 33] changes observed are mostly due to oxygen.



**Figure 4.1** Image of triangular pattern present on the surface

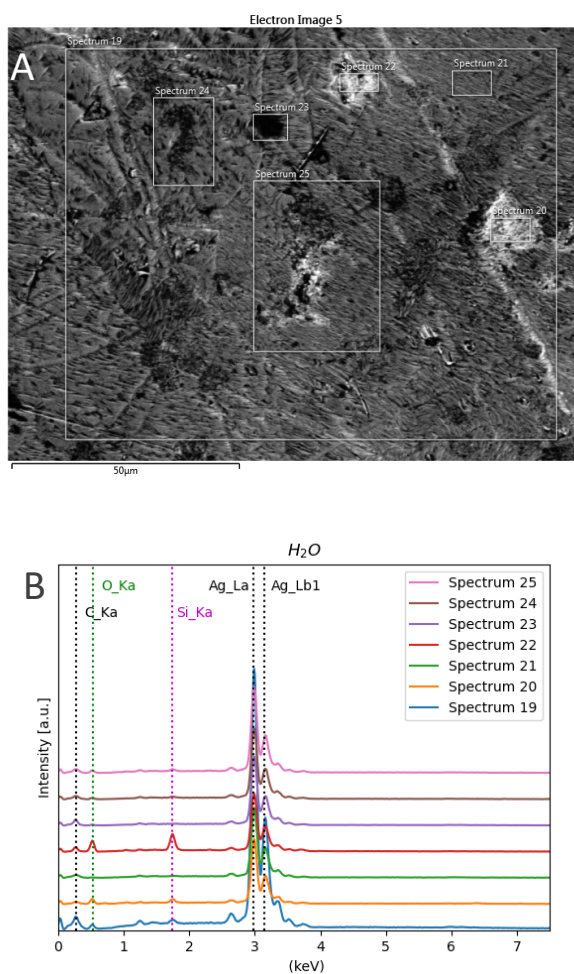


**Figure 4.2** Surface evolution of the silver catalyst under water vapour containing atmosphere. Where A, B – fresh; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. ( $T_{\text{bed}} = \sim 620^{\circ}\text{C}$ )

### 4.1.2 EDX results

The EDX was conducted after each experiment to evaluate the composition of the sample as well as analyse any artifacts that may have appeared on the surface of the catalyst.

The EDX investigation of fresh catalyst have shown that the catalyst is mostly pure silver with minor amounts of carbon, oxygen, and silicon. Silicon impurity may come from the vessel that the catalyst was stored in. When the catalyst was investigated after 84h experiment, more impurities have been detected. The main impurities found on catalyst surface are carbon, oxygen, and silicon in greater amounts. The silicon present on the spent catalyst can be attributed to as mentioned the vessel catalyst was stored, the quartz reactor the reaction took place or the glass wool surrounding the entry point to the reactor to keep the temperature in the reactor.



**Figure 4.3** The results of EDX analysis of the catalyst under water vapour - oxygen atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.



## 4.2 Syngas results

Since both CO and hydrogen are produced during the process as shown in equations 1, 4, 6 and 7 in point 2.1, the need to investigate the effect of both of those components on silver catalyst in presence of oxygen was relevant.

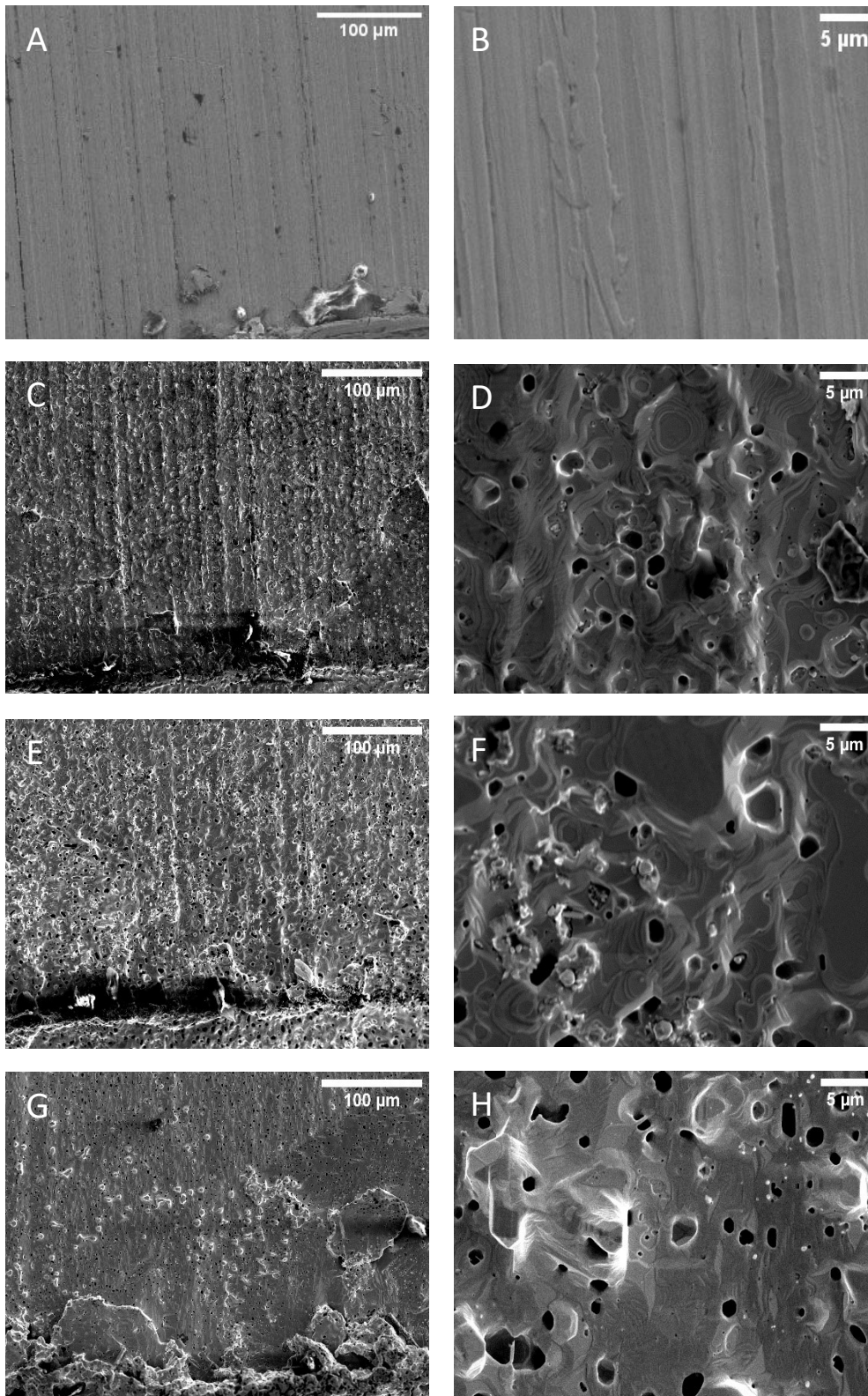
### 4.2.1 SEM images

High degree of surface change was expected from the syngas and oxygen atmosphere because both CO – oxygen and Hydrogen – oxygen atmospheres, influenced the surface structure to quite a degree as seen in specialization project [9]. In general, it was expected that the surface of the catalyst will look like the mixture of both effects with some having more effect than other. This assumption was correct as it is seen in the figure 4.4.

As it can be observed the change in the surface structure is quite dramatic between fresh and 12h experiment. The general view of the surface looks like the hydrogen oxidation experiment conducted in the specialization project [29]. The big holes that can be observed appearing on the surface of the catalyst can be attributed to the water formation according to the literature [32, 33, 34]. Literature proposed that both oxygen and hydrogen dissolve on the surface and when the hydrogen and oxygen atom meet, they can create a hydroxyl group which then can react with another hydroxyl group producing water molecule and free oxygen atom inside the crystal.

But when we go further down on the magnification scale, we can see the terracing which was most common to the carbon monoxide experiment [29]. What was also observed is that small crystals started to appear on the surface as well as in the holes and pinholes as the experiments have progressed. Crystals appearing on the surface were also common to the sample exposed to CO – oxygen atmosphere. The identification of this crystals will be presented in the EDX subsection.

Additionally, the ability to find the same areas on the catalyst surface became more difficult with each experiment because of the extensive surface transformation.

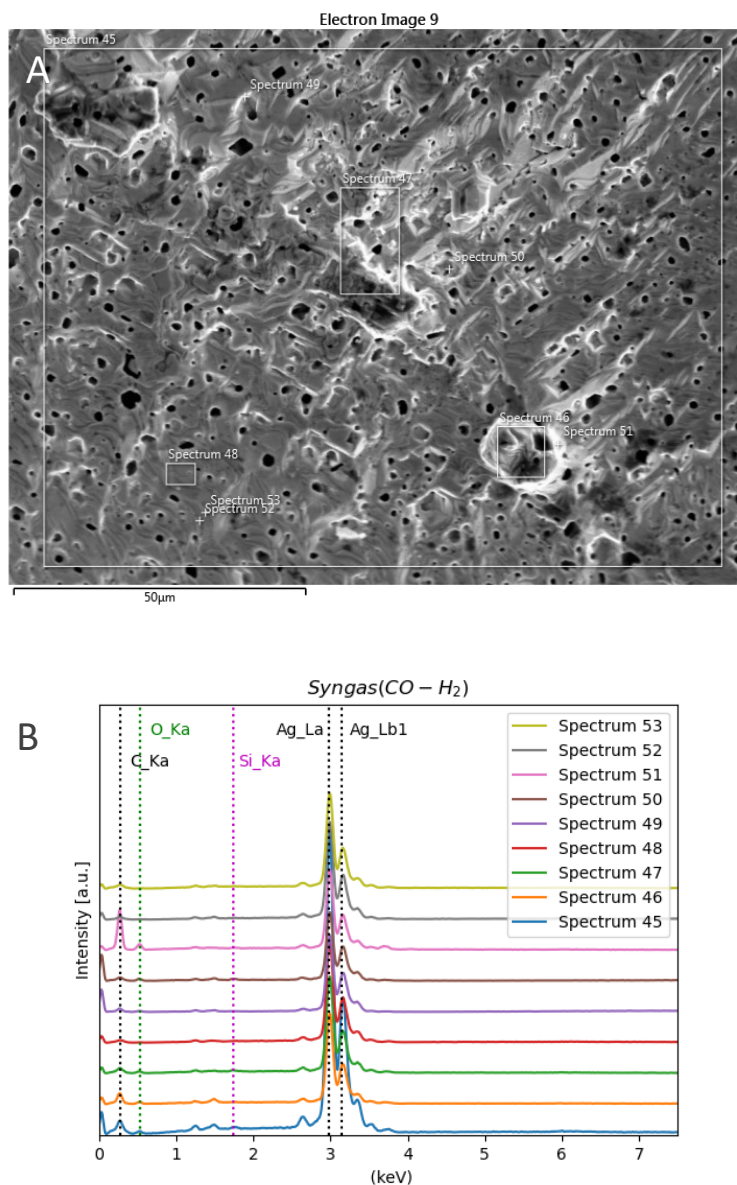


**Figure 4.4** Surface evolution of silver catalyst under syngas-oxygen atmosphere. Where A, B – fresh catalyst; C, D – after 12h; E, F – after 36h; G, H – after 84h. ( $T_{\text{bed}} = \sim 620^{\circ}\text{C}$ )



### 4.2.2 EDX images

EDX investigation of syngas catalyst have shown that due to severe surface change it was difficult to obtain reliable data from the surface. Since the surface had some many holes and artifacts the EDX program gave false spectra that had to be eliminated. The results of the EDX investigation can be seen in the figure 4.5.



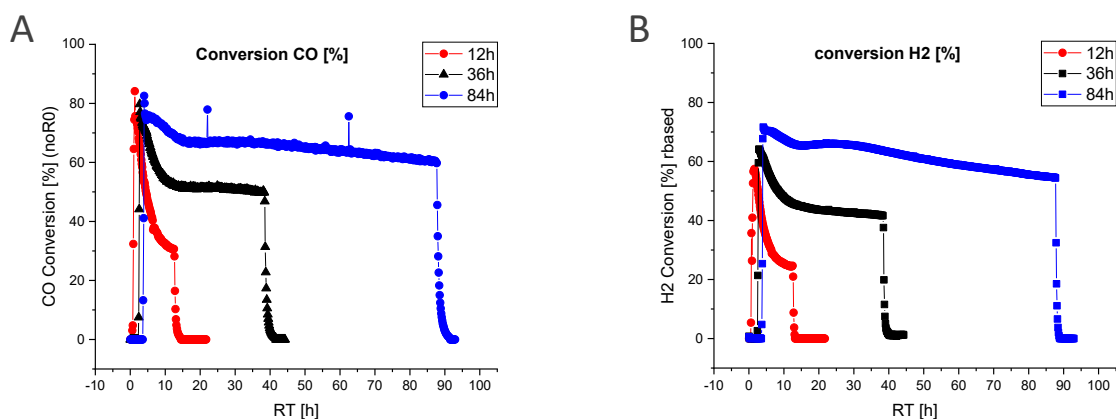
**Figure 4.5** The results of EDX analysis of the catalyst under syngas- oxygen atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.

As it can be seen the surface is dotted with holes and small crystals. During the EDS investigation the crystals were identified to be made of silicon, oxygen and carbon. The origin of the silicon on the surface can be explained due to the transmission from the glass wool that serves as an insulator to the lines and reactor, also the housing of the sample was made of quartz which allows the introduction of this impurity highly likely. Carbon present in the sample is proving to be more difficult to predict its origin. Carbon could be attributed to carbon deposition from CO present in the feed or it could be the carbon that was already present within the catalyst matrix. During the restructuring of the surface this

impurity segregated to the surface and agglomerated. Normally such carbon should react with oxygen present.

### 4.2.3 Activity

The conversion results gathered from the syngas experiments proved to be quite surprising. The results can be seen in the figure below.



**Figure 4.6** Comparative graphs showing the conversion of both CO (A) and Hydrogen (B) during the experimentation period. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

Figure 4.6 shows that the conversion in subsequent series of experiment have been increasing for both CO conversion and hydrogen conversion after each experiment. Additional observation that can be made is that the activity of the catalyst tends to stabilize around 70% with each next experiment in the series.

The combination of kinetic results from the experiments and SEM images from the same series of experiments are giving interesting hypothesis. During the experiment, the surface of the catalyst is going through a period of profound change. If coupled with the increase in conversion, it could be interpreted as the hydrogen present during the oxidation of carbon monoxide increases its conversion as well as the conversion of hydrogen itself. Additionally, the increase in conversion can be attributed to the holes formation on the surface. When water molecule is formed on the surface it leaves a hole behind as stated by literature [32, 33, 34], it uncovers fresh catalyst material. This fresh material then can be the new site of interaction for the CO molecule to attack.

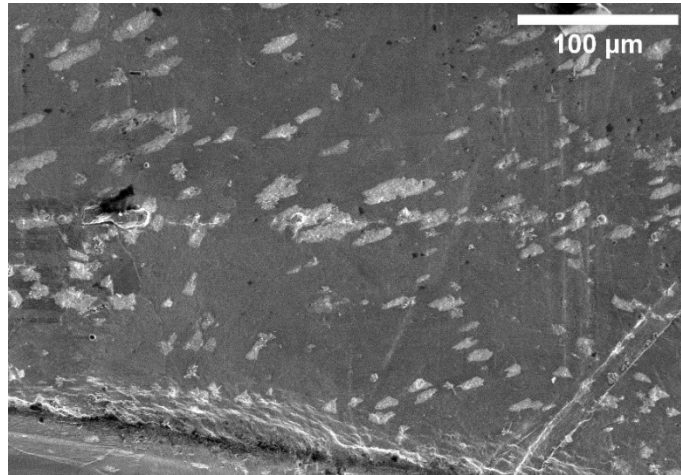


## 4.3 CO-water oxidation results

The large amount of water is added to the MTF process. Water-oxygen effect on the surface was already analysed. The effect of water presence in the CO-oxidation was an interesting idea to investigate, given that they both are present during the MTF process.

### 4.3.1 SEM results

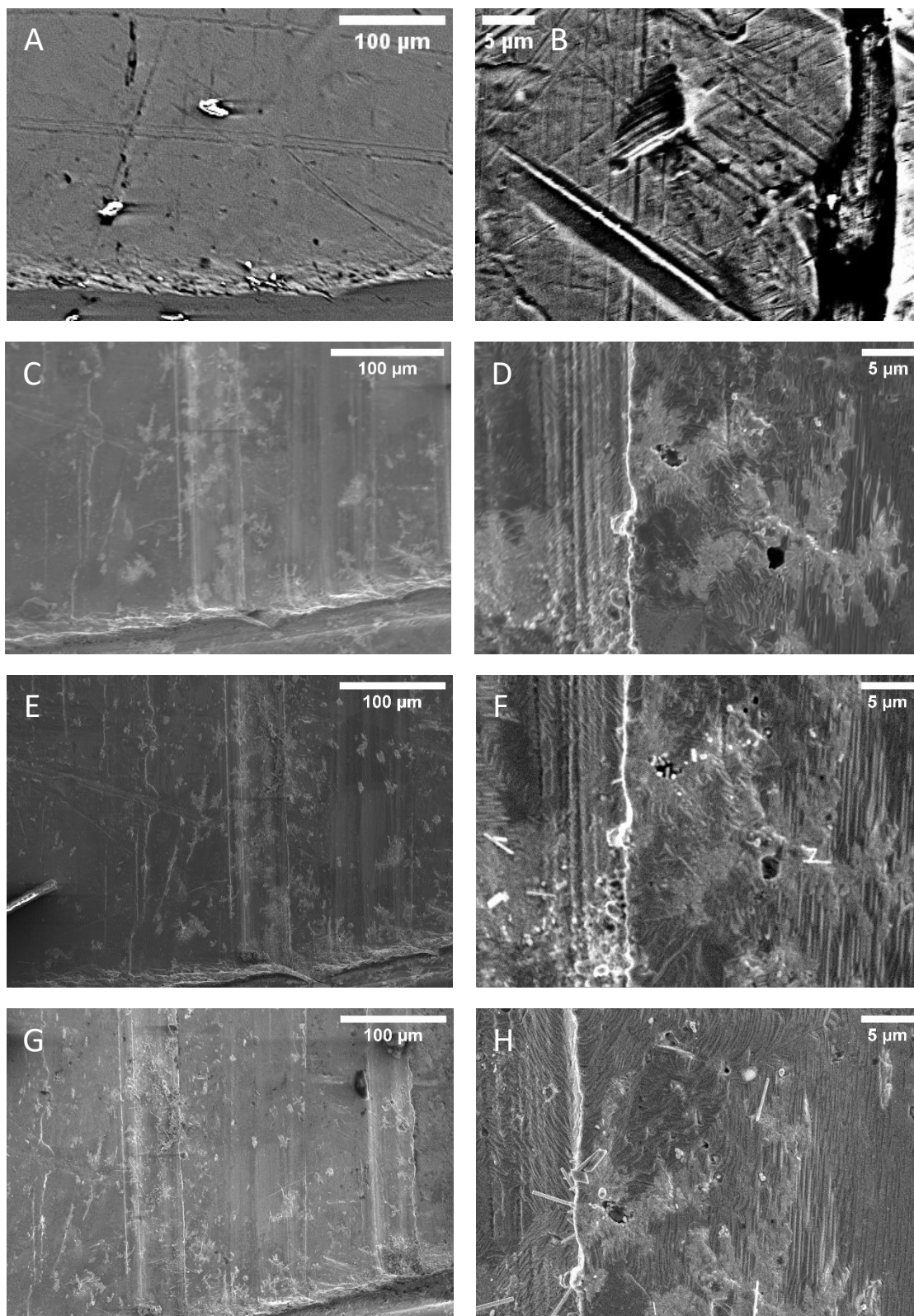
As in the previous experiments, the expectation was met. It was assumed that the changes done to the surface will be a mixture effects of components of the mixture. The assumption was proved correct. The evolution of the surface can be observed on the figure 4.8.



**Figure 4.7** The white spots present in the catalyst subjected to CO – water vapour atmosphere. ( $T_{bed} = \sim 620^{\circ}\text{C}$ , 84h experiment)

The surface of the catalyst at the end of experiment period evolved into the stepped-like formation on the surface. Additionally, some triangular pattern was present at some places in the investigated areas. The stepping effect on the sample was observed in the sample that was subject to the CO-oxygen atmosphere [29] and the triangular pattern of surface change was more seen in the water exposed sample as well as in experiment done by Millar et al. [30]. The combination of the effect was expected but the appearance of white spots as shown in figure 4.7 was an interesting finding.

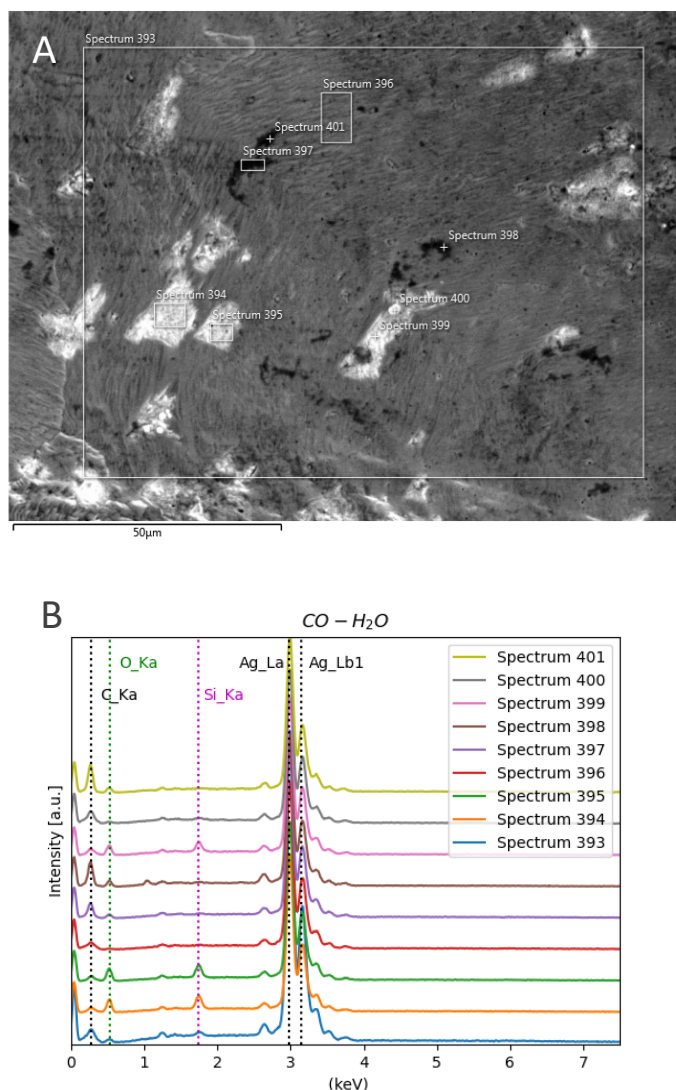
The amount of the white spots appearing on the surface was not seen in previous samples on such a scale. Yet it also needs to be mentioned that fractal-like pattern of growth was observed on some sites of the catalyst. That was an interesting observation since no previous sample has exhibit such a behaviour and triangular pattern was also observed around this fractal-like growth. Given that the heat dispersion created by water vapour and presence of oxygen, enables this kind of formation to grow with the addition of CO in the atmosphere.



**Figure 4.8** Surface evolution of silver catalyst under CO-water vapour-oxygen atmosphere. Where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

### 4.3.2 EDX results

During the EDX of this sample the identity of white spots on the catalyst surface was found as mentioned in previous subsection. The overall results of the EDX can be seen in the figure 4.9.

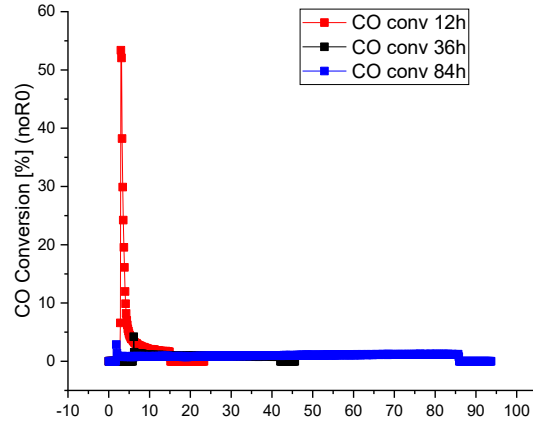


**Figure 4.9** The results of EDX analysis of the catalyst under CO-oxygen-water vapour atmosphere after 84h. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.

As can be seen in presented graph the white spots are mostly made of silicon and oxygen with sometimes the addition of calcium and carbon present also. The black spots can also be seen on the surface which were identify as carbon containing material with some oxygen and silver present. Due to using 20 keV during the investigation the degree of surface penetration is high which would explain why in the white and black spots we spot silver. Additionally, some long rods of glass wool have been observed on the catalyst surface. The rods probably came from the insulation of the reactor which is made of glass wool.

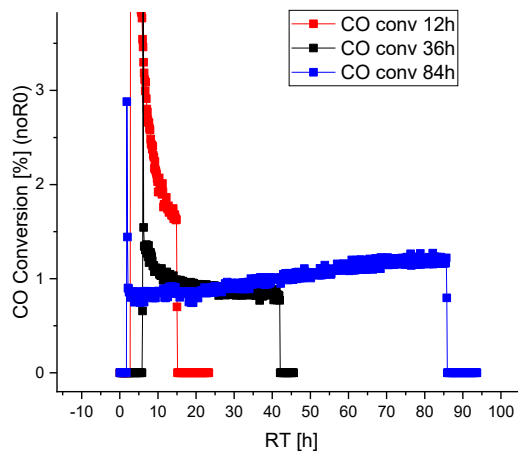
### 4.3.3 Activity

Kinetic data was collected during the entire experimentation period which can be observed in the figure 4.10.



**Figure 4.10** Graph showing conversion of CO during investigation period. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

The graphs present an interesting result, the observation can be made that water added to the CO oxidation mixture reduces conversion significantly. As shown in the graph first we have high conversion peak which is immediately followed by drop in conversion to 1%. The next series of experiments namely 36h and 84h ones shown that the high peak is never attained after the 12h experiment. It can also be seen that these experiments shown a tendency to stabilise around 1% percent conversion. This can be shown in figure 4.11.



**Figure 4.11** The zoomed in area of the graph of CO conversion during CO-water oxidation

This could imply that water added to the mixture has potential to CO oxidation reaction on silver, while the addition of hydrogen promotes it as seen in in figure 4.6. Furthermore, this could indicate that water added to the mixture has potential to stop side reactions in MTF process as shown CO-oxygen-water experiment.

## 4.4 Hydrogen and water experiments

The previous series experiments were investigating the effects of water addition on CO oxidation and the results received from them proved interesting. So, it was recommended to perform the hydrogen oxidation with water. This investigation can show how water affects the reaction and if the effect is similar to CO-water oxidation.

### 4.4.1 SEM results

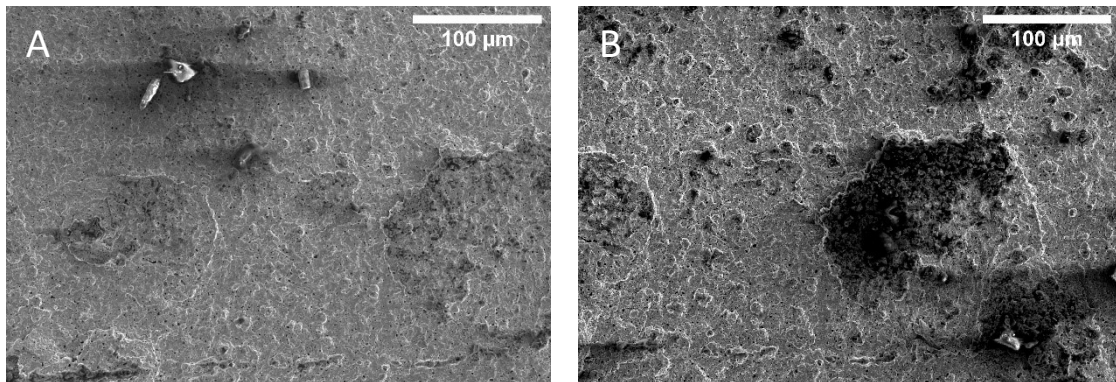
The figure 4.13 presents the evolution of the surface during experimental period.

The changes observed in figure 4.13 have similarities to changes of surface observed in hydrogen oxidation [29] as well as in Lervold et al. [35]. Additionally, the structure of the surface bears similarity to the MTF effects on the surface presented in Lervold et al. [28] and Nagy et al. [36].

It can be observed that initially the plateau-like formation presents on the surface with holes which are the results of hydrogen absorbing, later reacting with absorbed oxygen and then desorbing water molecule.

As the experiments have progressed the holes became bigger, and the plateaus have lost their initial shape becoming more amorphous looking with each experiment.

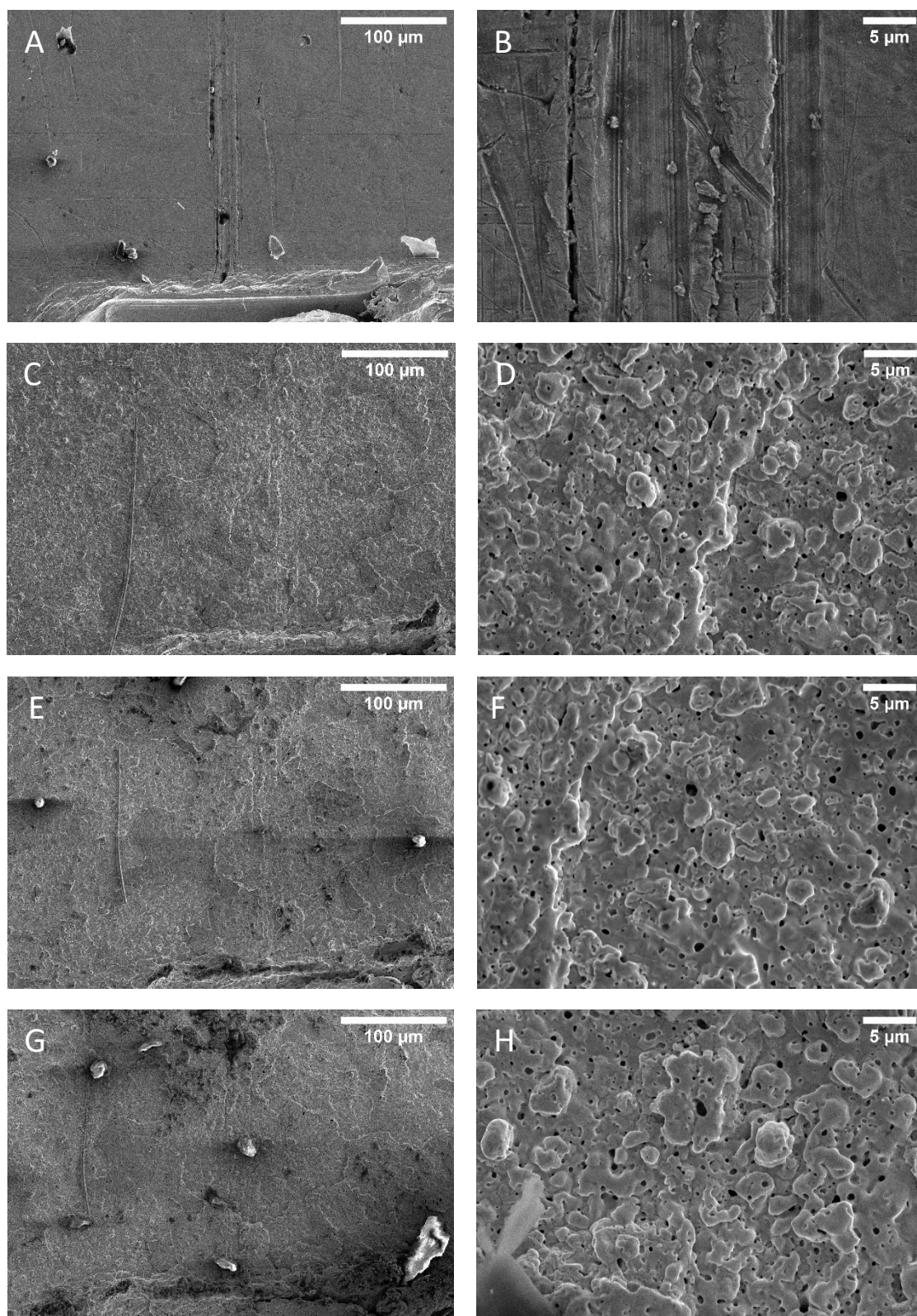
What also can be observed is that with each experiment the black matter is appearing in larger quantity on the surface of the catalyst. What also can be observed is that the amount of the black material covering the surface has been increasing with each experiment.



**Figure 4.12** The growth of the black matter on the catalyst surface. Where A - after 36h and B - after 84h.

As it can be seen in the figure 4.12, the growth of the black matter was extensive. The black matter seems to agglomerate in specific areas as shown in figure 4.12. Additionally, the increase in amount of black stuff can be seen in figure 4.13 and Appendix D.

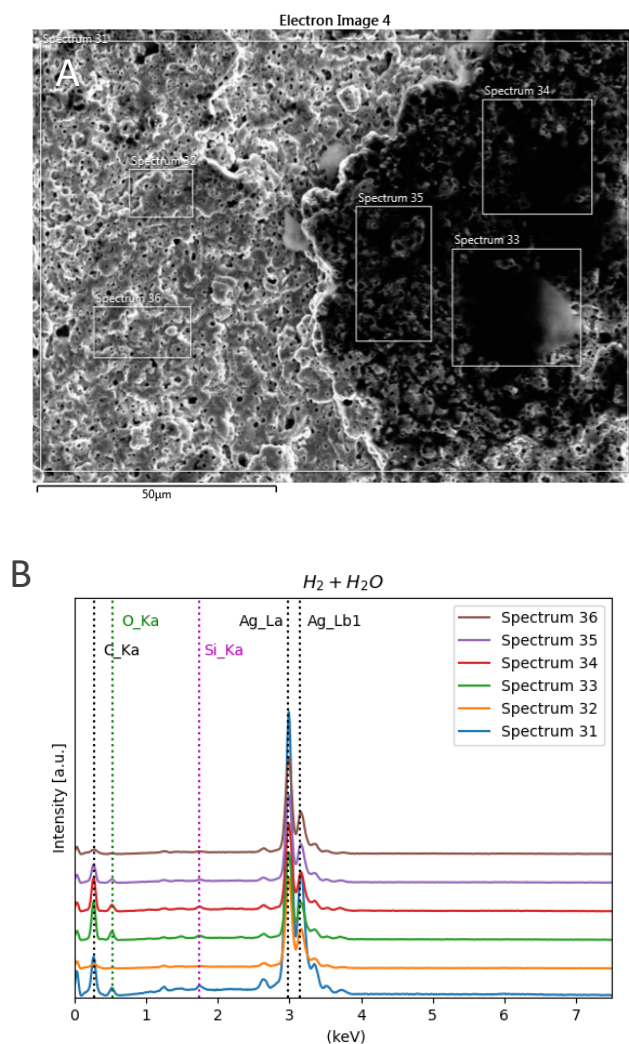




**Figure 4.13** Evolution of the catalyst surface under Hydrogen-oxygen-water vapour atmosphere where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

#### 4.4.2 EDX results

Given that the black spots have been observed the need to investigate its identity was a logical step. As it can be observed in figure 4.18 B, the black stuff on catalyst surface was determined to carbon. The presence of carbon was a somewhat surprising due to the oxidizing atmosphere of the experiment conducted and lack of carbon species in the feed. Oxidizing atmosphere and high temperature are known in industry to be great carbon removals from catalyst surface. Additionally, as shown in fig 4.18 A the carbon present on the surface have a sponge-like appearance.

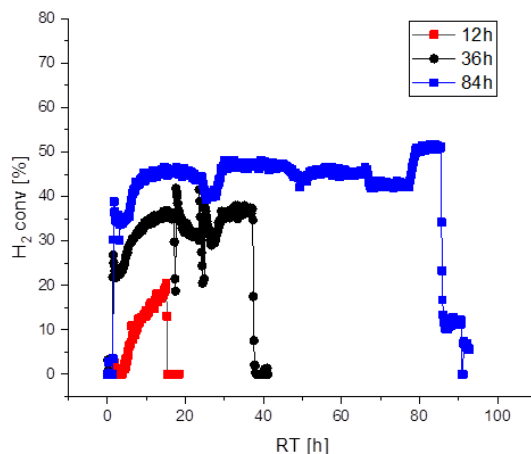


**Figure 4.14** The results of EDX analysis of the catalyst under hydrogen – water vapour - oxygen atmosphere after 84h experiment. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.

Given the fact that the reaction atmosphere did not contain any carbon species, carbon could have originated from the matrix of the catalyst. This could imply that the catalyst had some carbon impurity before the experiments have started.

### 4.4.3 Activity

The conversion of the hydrogen during experiments is presented in the fig. 4.15.



**Figure 4.15** Conversion graphs for the Hydrogen oxidation in the presence of water vapour. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

As shown in figure 4.15, hydrogen oxidative conversion presented quite an interesting behaviour. Initially there was low conversion that gradually rose over the course of experiment. Which is also worth noting is that next experiment starts higher than the previous similarly to the behaviour present in the syngas oxidation. What also can be observed that with each following experiment in the series the activity of the catalyst tends to stabilize around 45% conversion level.



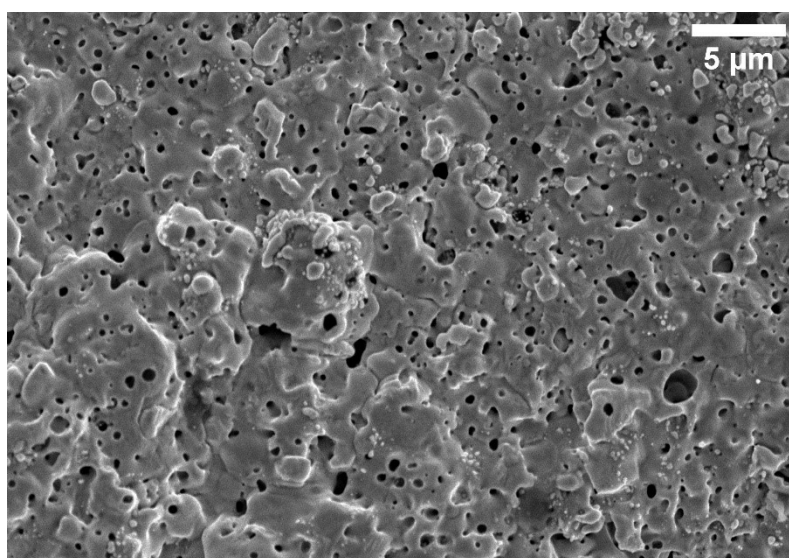
## 4.5 Syngas and water experiments

To complete the investigations of variety of different atmospheres and their interaction with silver, the Syngas-oxygen-water vapour atmosphere was chosen.

### 4.5.1 SEM results

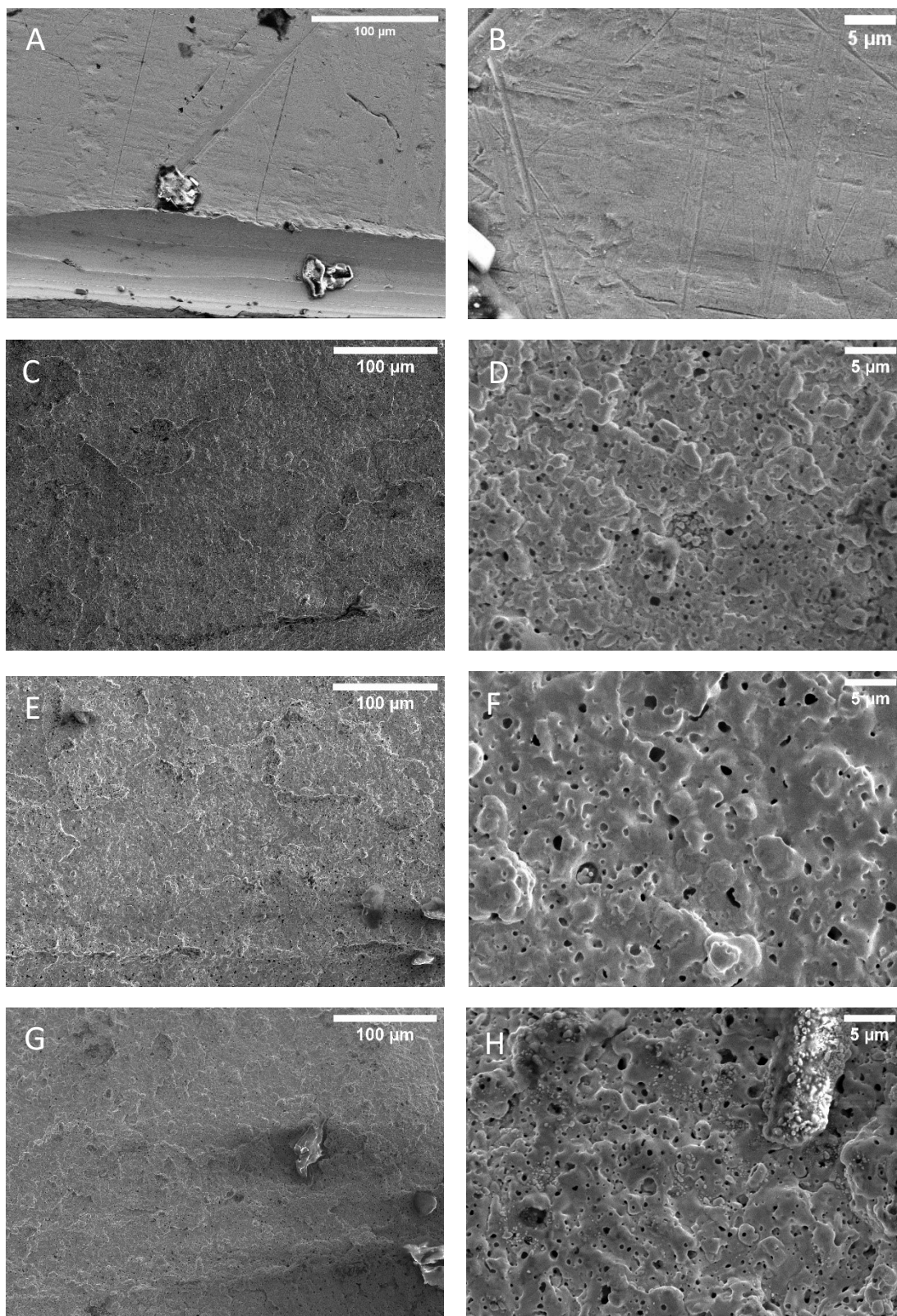
Since the study of the effect on surface for mixtures of CO-hydrogen-oxygen, CO-oxygen-water and H<sub>2</sub>-oxygen-water was already done, the investigation of CO-hydrogen-oxygen-water mixture seemed to be next logical step. As previously the mix of effects on the surface was expected but the results were interesting. The surface evolution can be observed in the figure 4.17.

The observed change from the image of the fresh catalyst to the 12h is quite severe. After the 12h period of experiment we can observe plateau-like formation on the surface with each experiment became more smoothed with increasing number of holes on the catalyst surface. The change presented in figure 4.17 resembles the change that the catalyst surface have gone through under MTF reaction conditions which were investigated by Lervold et al. [28] and Nagy et al [36]. The reaction atmosphere in this investigation is approaching the composition that is used in the Methanol to formaldehyde process aside from the methanol and formaldehyde.



**Figure 4.16** The small crystals present on the surface of the catalyst.

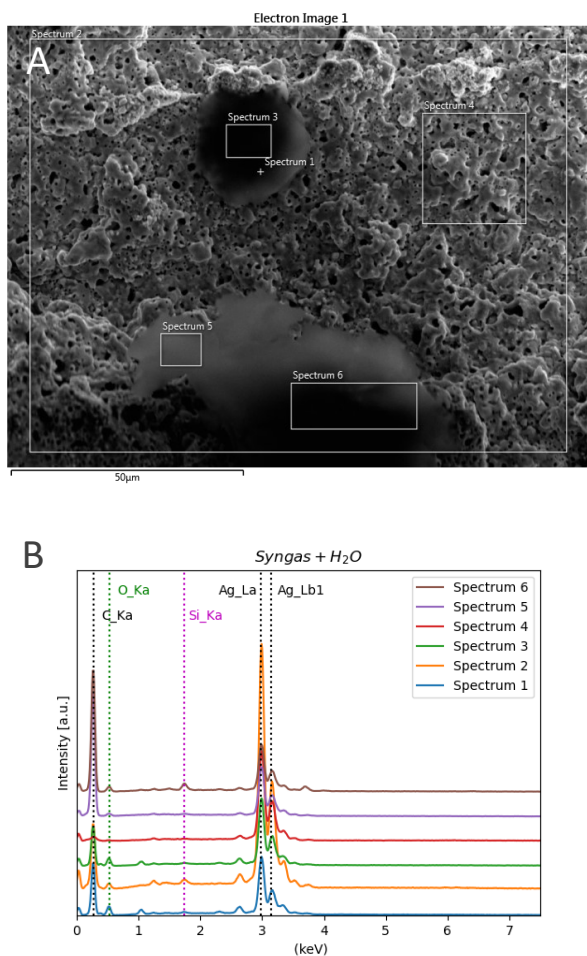
As shown in figure 4.16 the surface of the catalyst was dotted with small crystal-like features. This formation can also be observed in figure 4.17 as well as the Appendix E. As it can be seen the crystal-like formation are seen in all investigated areas which look similar to those which were observed in the investigation of CO oxidation without adding hydrogen and/or water [29]. The crystals could have splintered out as part of the reconstruction process. But the definitive origin of those crystals is still unknown.



**Figure 4.17** Evolution of the catalyst surface under Syngas-oxygen-water vapour atmosphere where A, B – fresh catalyst; C, D – after 12h experiment; E, F – after 36h experiment; G, H – after 84h experiment. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

### 4.5.2 EDX results

In the EDX investigation of this catalyst the two black shapes were discovered and analysed. The results can be observed in figure 4.18.



**Figure 4.18** The results of EDX analysis of the catalyst under syngas – water vapour - oxygen atmosphere after 84h experiment. Where A – image of investigated area with markings of the spectra, B – graph showing off spectra obtained.

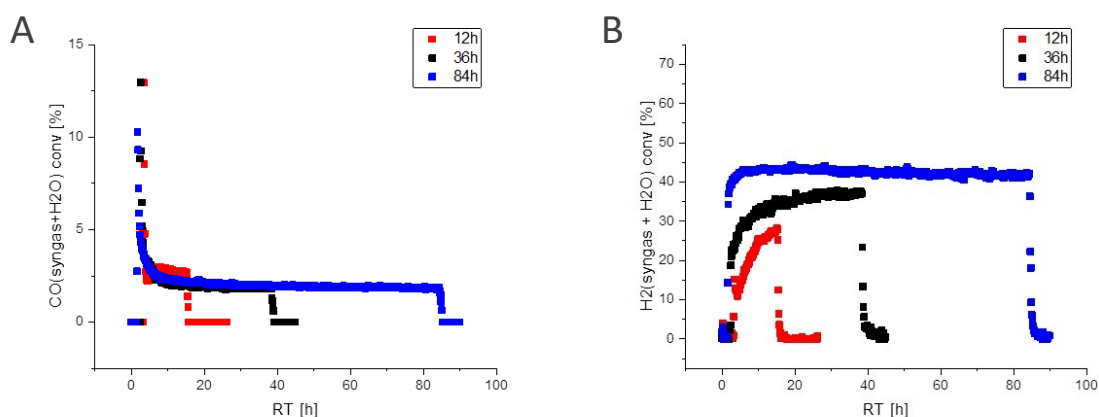
As we can see in the figure 4.18 B which represents the collected spectra, the EDX have shown that the black spots consist of mostly carbon, some oxygen and silver. The carbon present on the surface can have multiple points of origin. The carbon could have come from the deposition of the carbon from the CO present in the feed stream. Alternatively, the carbon was already present in the catalyst and during the experiments it has accumulated and migrated to the surface during reconstruction. But what was surprising is the fact that the carbon did not react in the presence of oxygen.

### 4.5.3 Activity

In previous paragraphs, the effect of hydrogen and water on conversion was presented separately and discussed. While these experiments have dealt with the syngas oxidation in presence of water. It was interesting to see what the addition of water would do to the activity of the catalyst, given that it was already seen how water affect CO-oxidation and hydrogen-oxidization separately.

The figure 4.19 shows the conversion of both the CO and hydrogen over the course of experimental period. Similarly, to the experiment concerning the CO oxidation in presence of water, the CO conversion follows the same pattern. The CO conversion curve in figure 4.19 shows that after initial peak of around 10% then its decreases to the around 3% and stays at that level till the end of experiment. This is another confirmation that the water could be responsible for interrupting further reaction of CO.

The hydrogen behaviour shown in the figure 4.19 bears resemblance to the hydrogen oxidation with addition of water. As in the hydrogen oxidation, initially there was low conversion that gradually rose over the course of experiment. Which is also worth noting is that next experiment starts higher than the previous similarly to the behaviour present in the syngas oxidation. What also can be observed that with each following experiment the activity becomes more stable in its behaviour.



**Figure 4.19** Conversion graphs for the Syngas oxidation in the presence of water vapour. Where A is CO conversion during experimental period and B Hydrogen conversion during experiments. ( $T_{bed} = \sim 620^{\circ}\text{C}$ )

## 4.6 Discussion

### 4.6.1 Temperature effect discussion

Given that all experiments performed have taken place at elevated temperature, its effect on the activity of the reactions in this study.

From the temperature data gathered it can be concluded that the isothermal conditions are preserved. This claim can be justified by almost constant bed temperature seen in all experiments. The bed temperature was measured by thermocouple placed inside of the quartz tube on the level of the catalyst.

Additionally, all reactants were heavily diluted during all of experiments presented in this study. The dilution of reactants limits the heat effect of those reaction.

The overall mass of silver used is large compared to the amount number of reactants. Silver also has very high thermal conductivity which implies that any hot spot that have appeared on the surface would dissipate across entire body of silver.

### 4.6.2 CO experiments overview

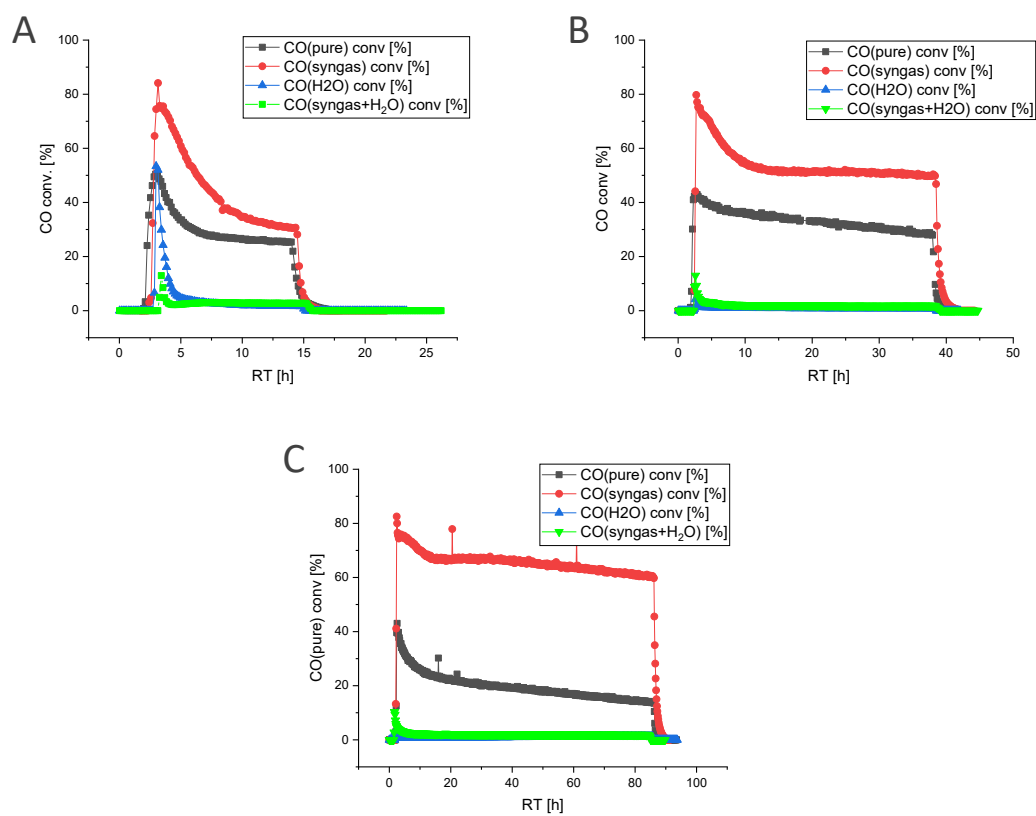
In this study the interaction of CO and other compounds have on the silvers surface was investigated. During those experiments, the CO conversion changed depending on the atmosphere it was in.

In the specialization project [28] the traditional CO oxidation was performed. The condition for that reaction were as followed: CO- 2mol%, O<sub>2</sub>-6mol%, and N<sub>2</sub>-92mol%. These experiments are the baseline conversion of CO on silver catalyst.

The next experiment conducted with CO-oxidation was its mix with hydrogen in 1 to 1 ratio, keeping the  $p_{CO}$  constant. As mentioned in section 4.2.3 the conversion increased in that atmosphere. The estimated increase is around 20 percentage points compared to the baseline CO conversion, as it can be observed in figure 4.20.

On the other hand, the effect of adding water vapour to a CO-containing oxidation limit heavily the reaction. The trend can be observed by following green and blue lines in the figure 4.20.

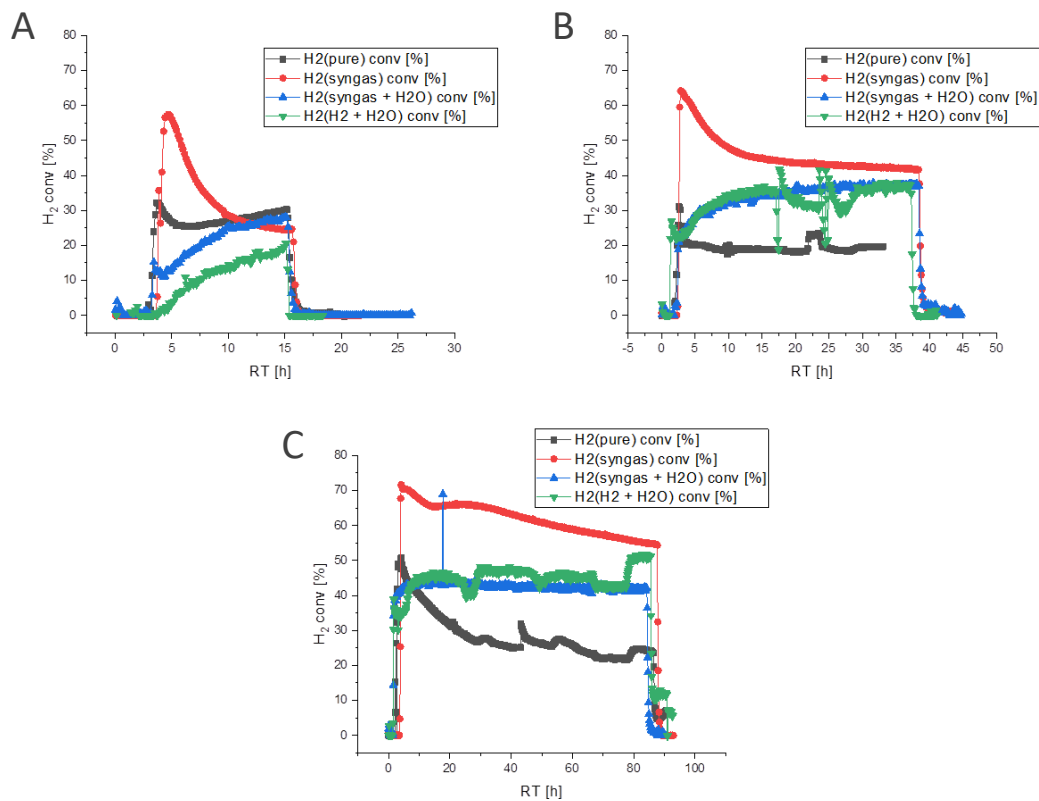
The reducing effect of water on CO conversion seems to be stronger than the enhancing effect of hydrogen in the overall conversion as seen in case of syngas + water vapour. Qian et al.[37] observed similar suppression in CO reactivity during main MTF reaction due to the presence of water in the feed. But given that in case of Syngas oxidation experiment water was one of the products which does not suppress the conversion.



**Figure 4.20** Comparison of CO experiment depending on the mixture. Where A – 12h experiment, B – 36h experiments and C – 84h experiments.

### 4.6.3 Hydrogen experiments overview

Similarly, to the CO experiments overview, the same can be done for hydrogen oxidation experiments. In this study hydrogen was present in different atmospheres giving a range of interaction and characteristics. Figure 4.21 shows the general overview and character of the experiments containing hydrogen in the reaction atmosphere.



**Figure 4.21** Comparison of hydrogen experiment depending on the mixture. Where A – 12h experiment, B – 36h experiments and C – 84h experiments.

As it can be observed in figure 4.21, the interaction of CO + H<sub>2</sub> + O<sub>2</sub> + water vapour atmosphere and H<sub>2</sub> + O<sub>2</sub> + water vapor atmosphere has very similar behaviour. The addition of CO in the syngas + water vapour case is most visible in 12h experiment graph A. The addition of CO to the hydrogen oxidation caused a large increase in activity as seen in red line in figure 4.21. From the experimental data it can be deduced that water has small suppressing abilities on hydrogen conversion as it has on CO. But the suppression disappears over time leading to a steady increase in activity.





# Chapter 5 Conclusion and future work

## 5.1 Conclusion

In this master's thesis, the effect of by products and feed elements of MTF reaction on the catalyst surface were investigated. The results are interesting and are shedding more light on the silver interaction during the main reaction.

Five experiments were conducted each having different atmosphere but each having the same amount of oxygen namely 6 mol% with varied other components. During each experiment, the surface of the catalyst was analysed to evaluate its evolution under given reaction atmosphere.

During the experiment with water and oxygen atmosphere the surface of the silver catalyst exhibited the tendency to create the triangular pattern on its surface. This evolution can be classified as mild change. The reason behind that classification is that the areas select for investigation after reactions were easily recognized and the scratch was still visible which allowed easy localization of the investigated sites.

Syngas experiments have shown dramatic surface change compared to water experiments as well as CO-water experiments. After 12h the surface has evolved quite heavily which was an interesting observation. With each syngas experiment the scratch made as a reference point became faded which made identification of areas difficult. But the resulting increase of conversion in CO oxidation by and addition of hydrogen was unexpected.

Even more interesting was the addition of water to the CO oxidation which resulted in virtually no conversion. This could indicate that water could be used to suppress to some extent the side reaction in the MTF process namely CO oxidation. To verify the water effect the experiment with syngas-oxygen-water atmosphere and hydrogen-water-oxygen atmosphere were conducted. In the syngas oxidation with water vapour the suppressing factor on CO oxidation was observed which again points into potential factor of CO reaction suppression. Additionally, on the surface plaster like structures have appeared that got more disfigured as the experiment proceeded. The final shape of the surface is reminiscent of the silver that have undergone MTF reaction. On the other hand, as shown in syngas oxidation with water vapour as well as hydrogen oxidation with water and hydrogen oxidation with water vapour present there was no suppressing factor on the hydrogen as it was seen in CO point of view. As shown in conversion graphs of these experiment the water enforces a peculiar shape of the curve in both syngas oxidation with water vapour and hydrogen oxidation with water vapour.

## 5.2 Future work

Based on the findings of this study, it could be beneficial to investigate other atmospheres and their effect on the surface. As shown in this investigation the atmospheres have a very distinct effect on the surface structure of the catalyst. Additionally, components of reaction atmosphere can have a strong effect on one another. This can result in different catalyst activity for the components of the mixture. Furthermore, it could be beneficial to investigate the kinetic aspect of the reaction presented in this study as well as other reactions that are present in the methanol to formaldehyde process. This approach may give insight into the mechanism of the MTF reaction, and the other processes involved in the reaction.

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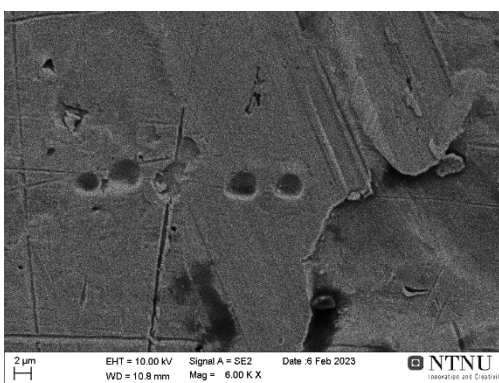
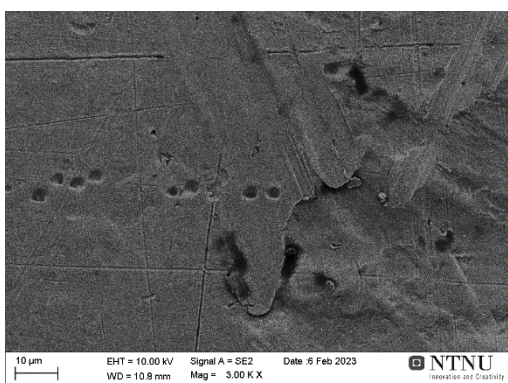
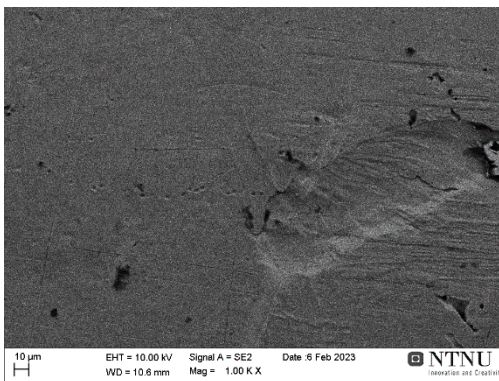
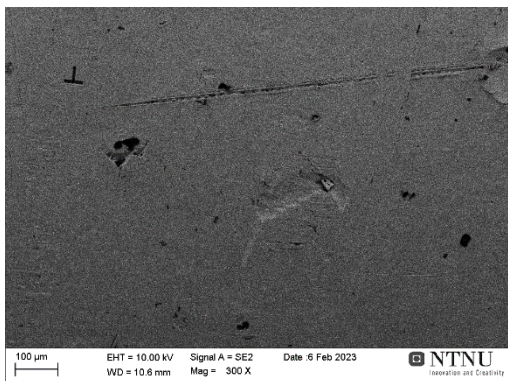




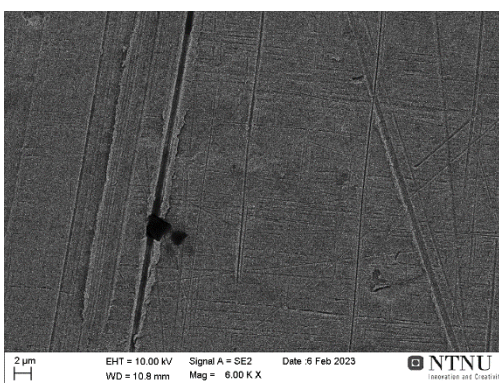
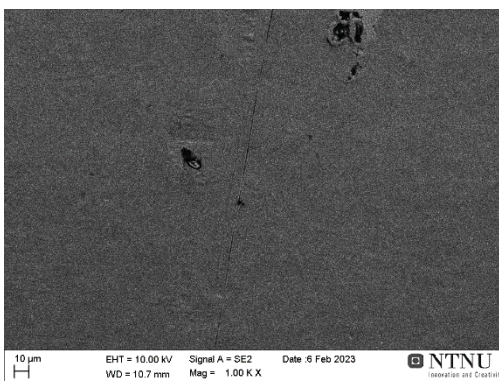
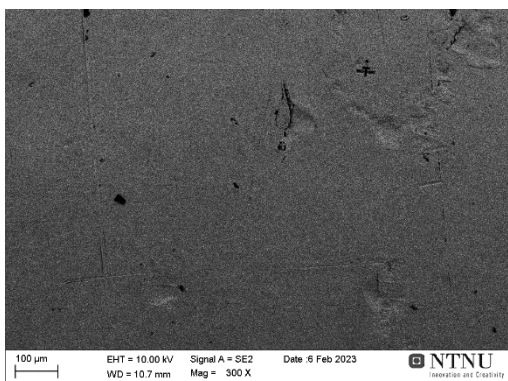
# Appendix A – Water-oxygen experiments

## 1. 12h experiment catalyst images

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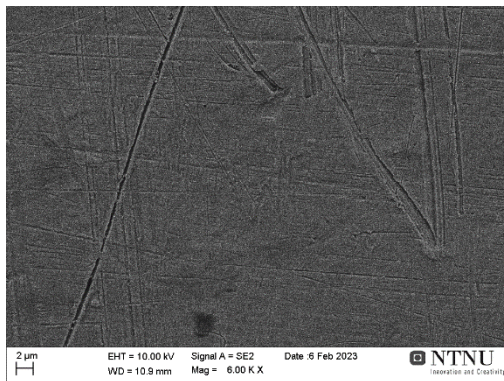
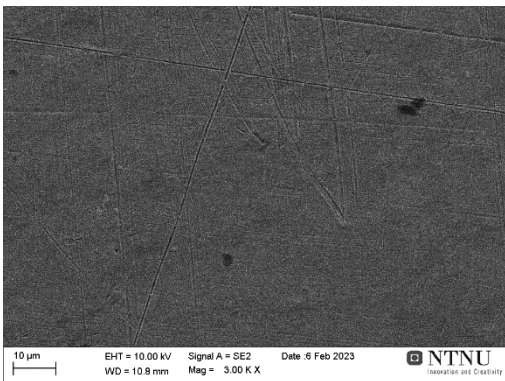
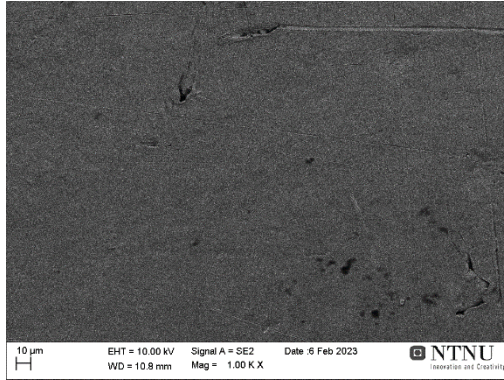
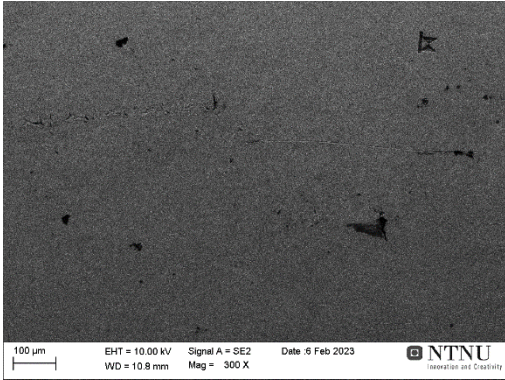


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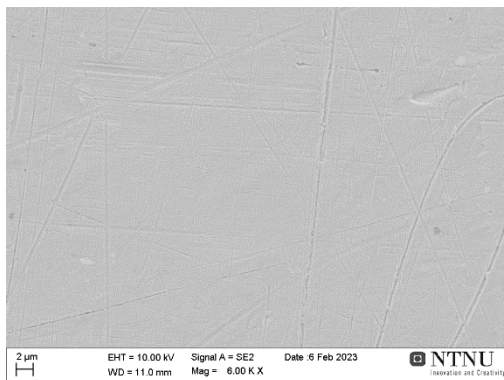
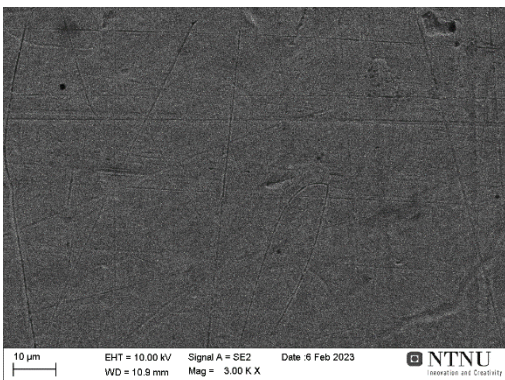
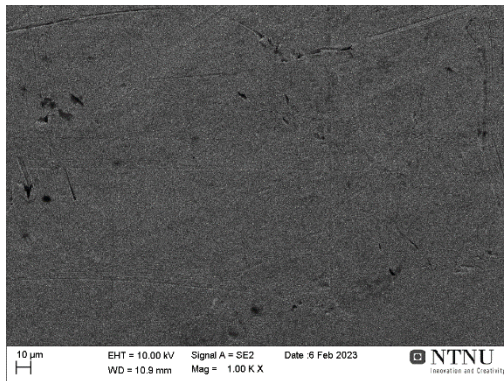
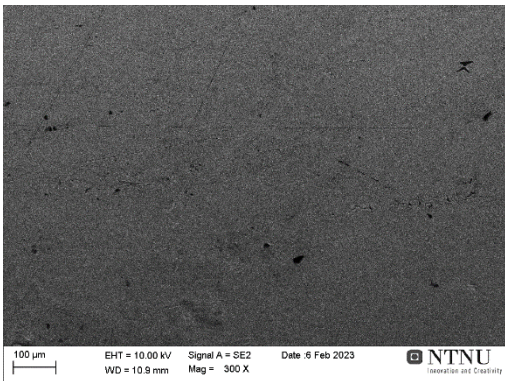




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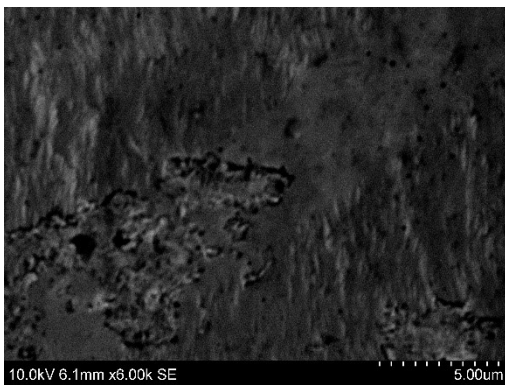
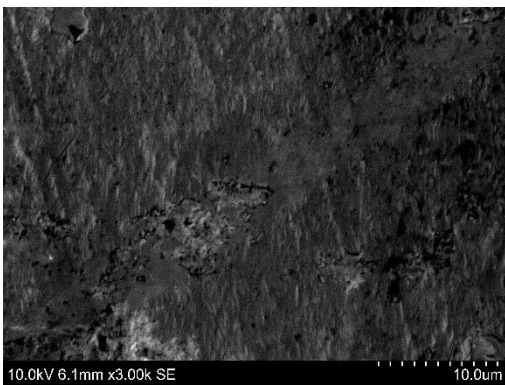
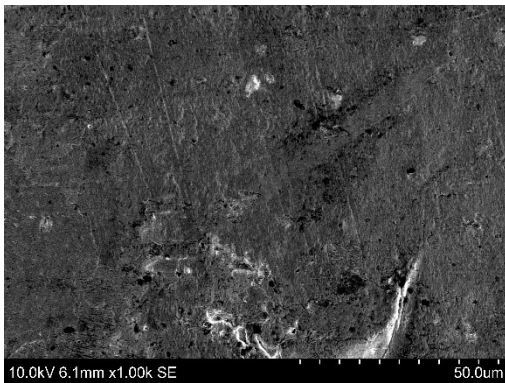
### D) Area 4



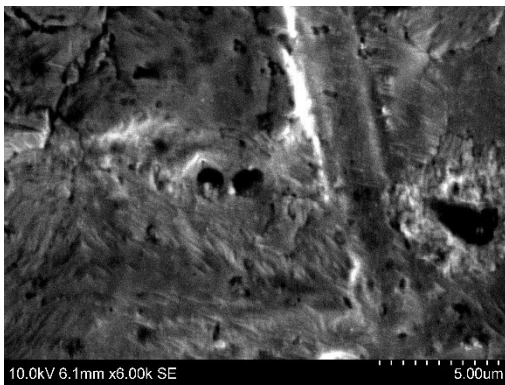
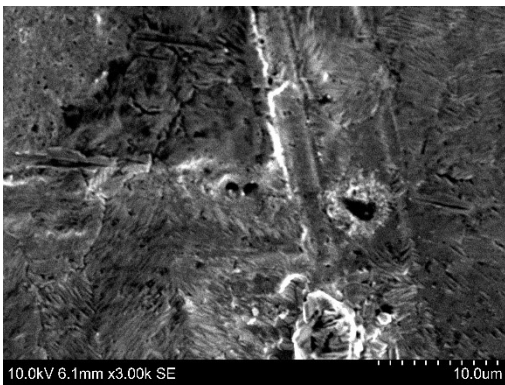
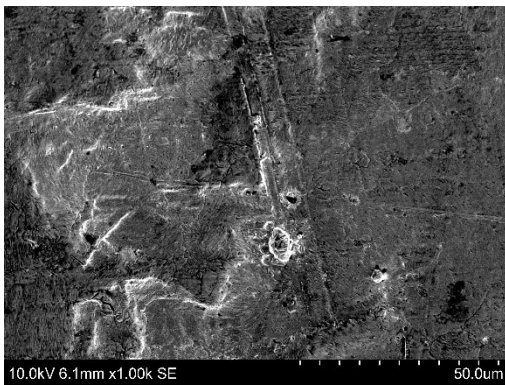
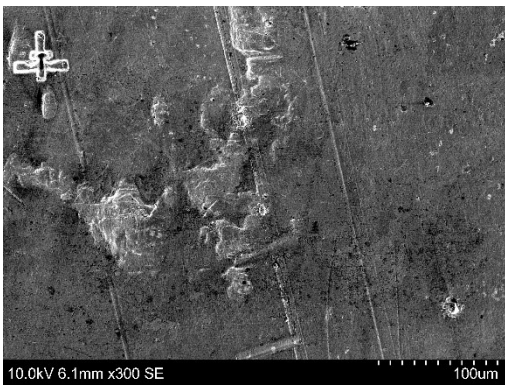


2. 12h experiment catalyst images

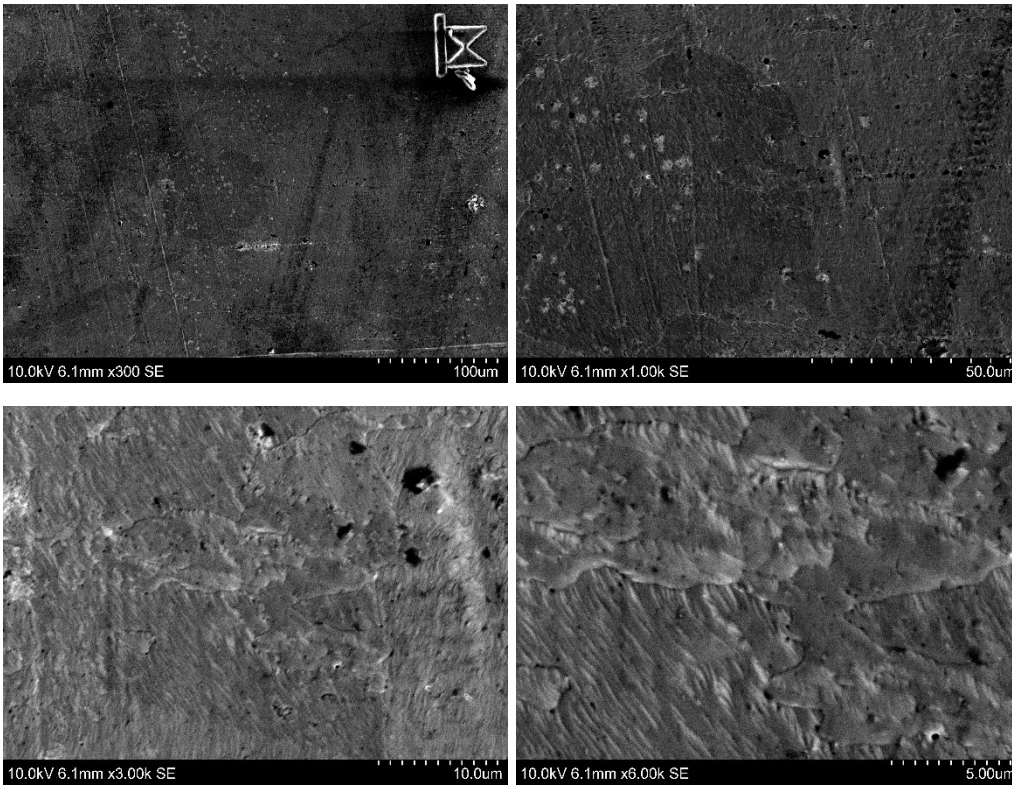
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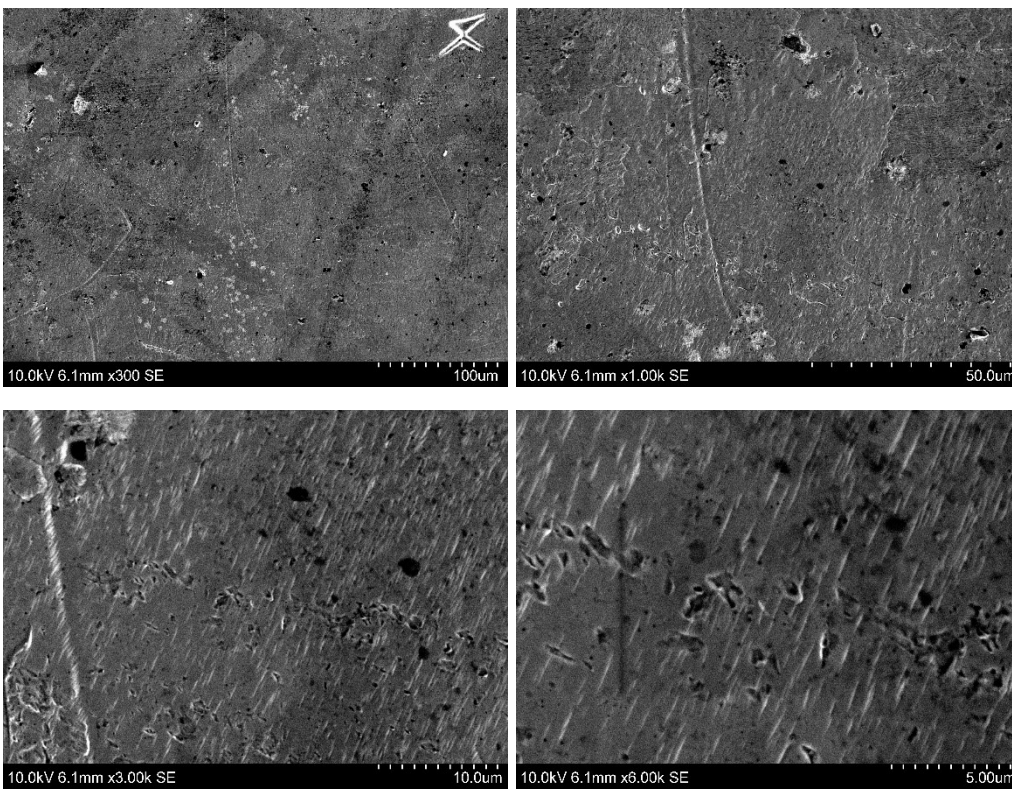
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C) Area 3

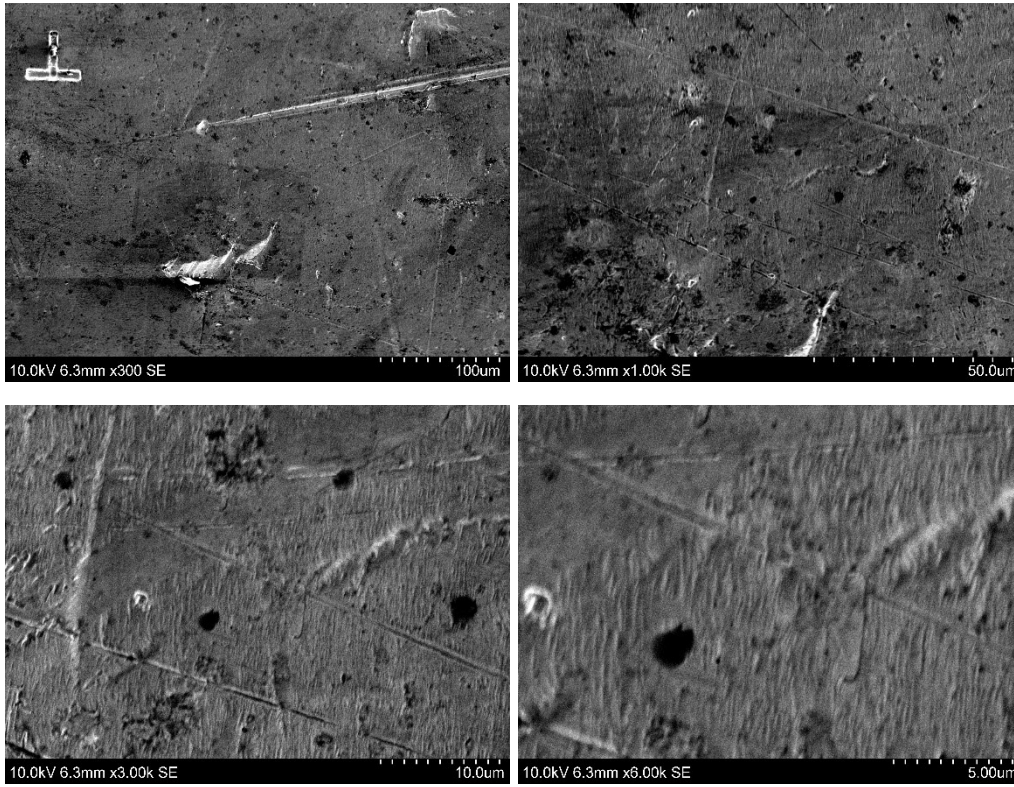


D) Area 4

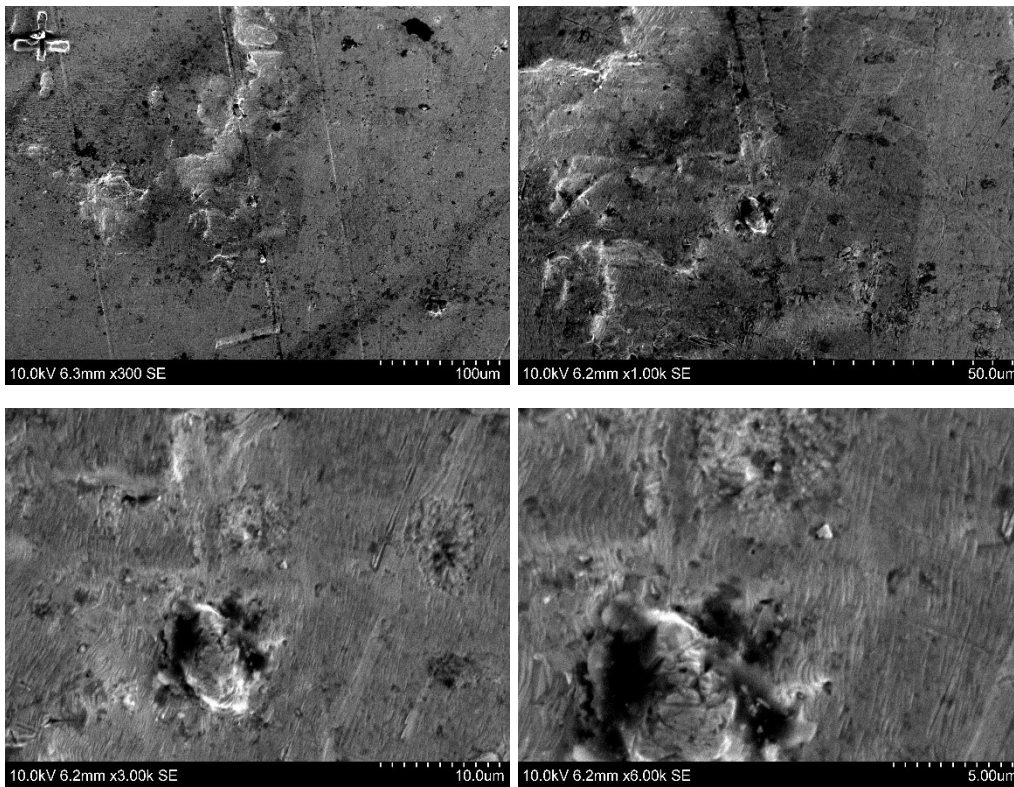


3. 36h experiment catalyst images

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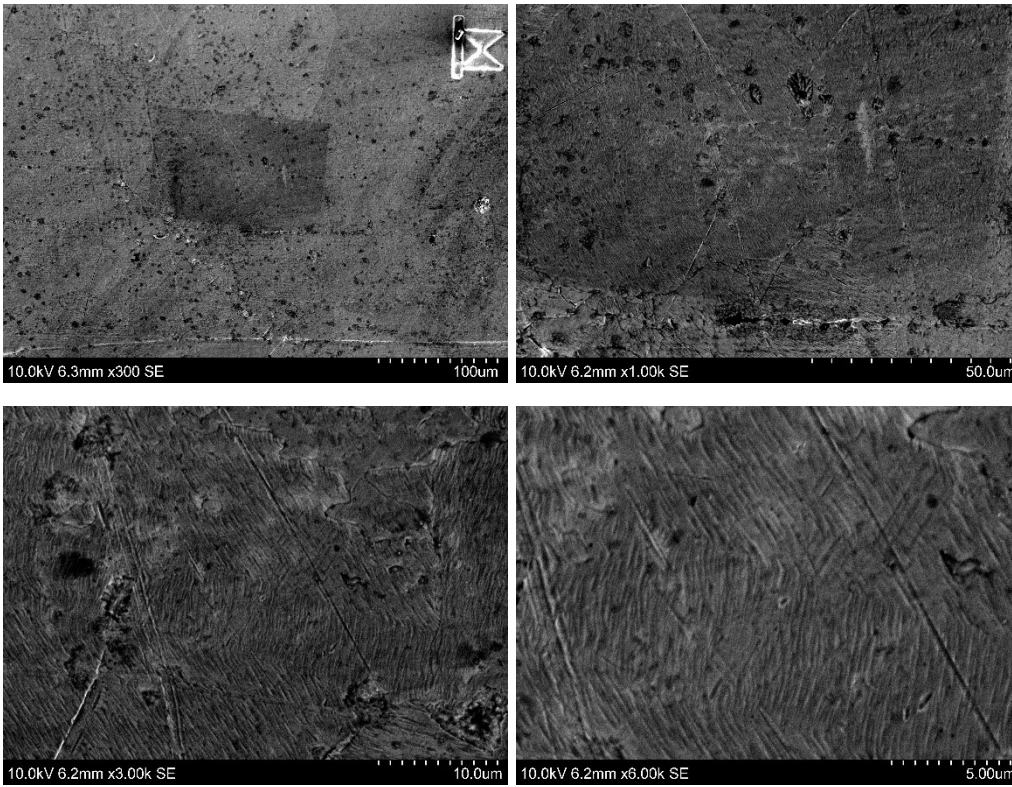


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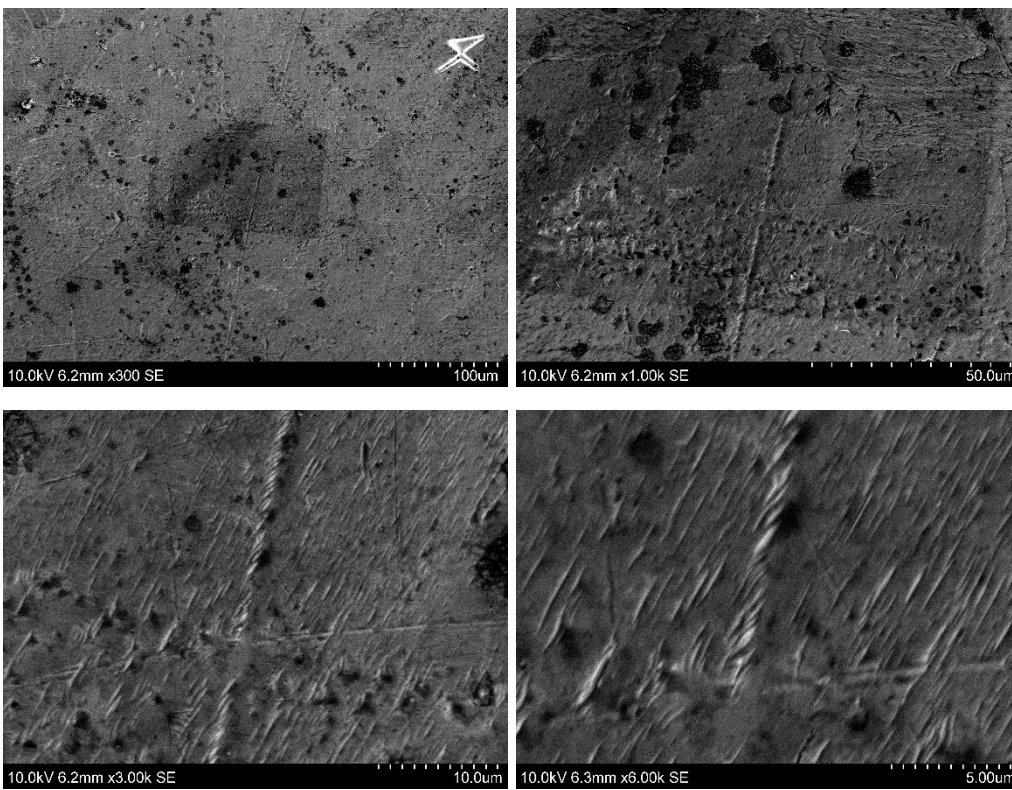




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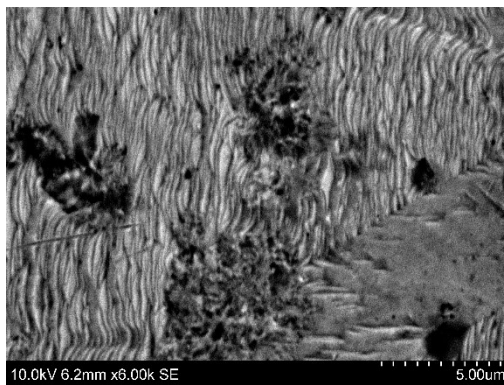
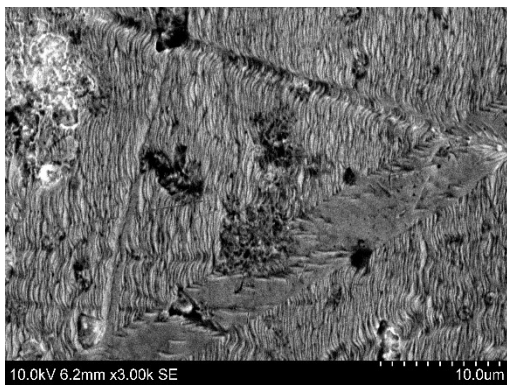
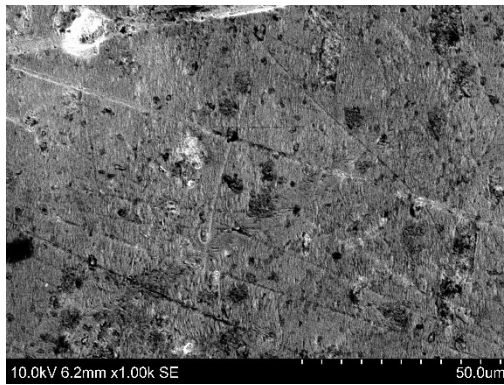
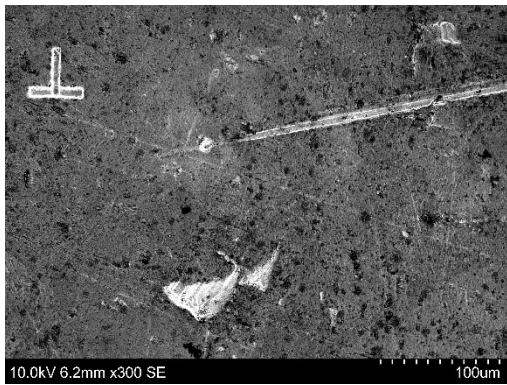


D) Area 4

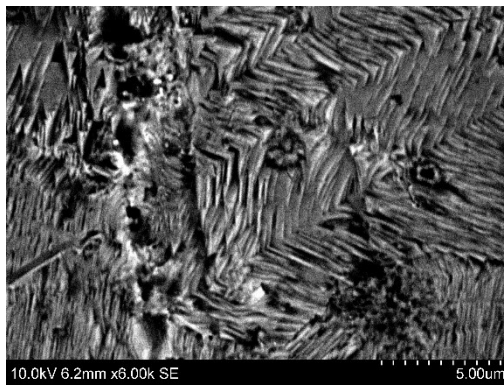
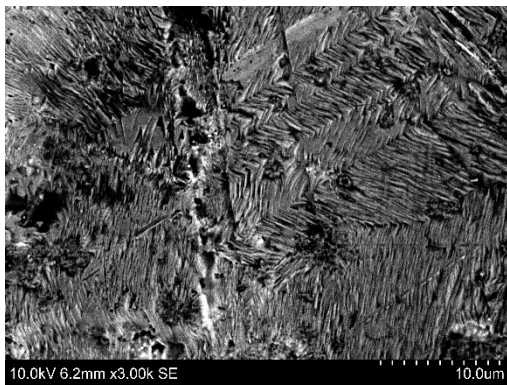
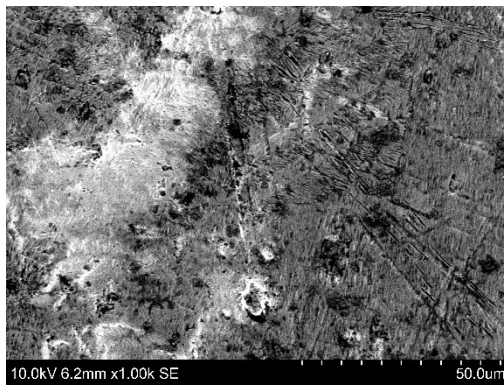
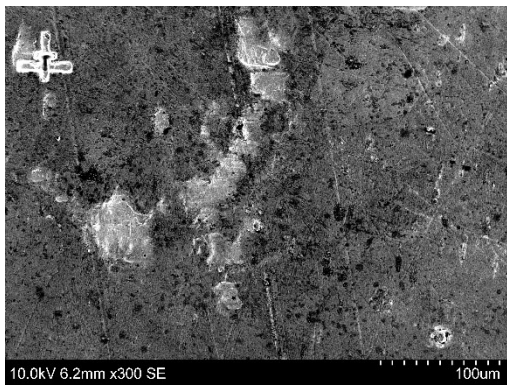


4. 84h experiment catalyst images

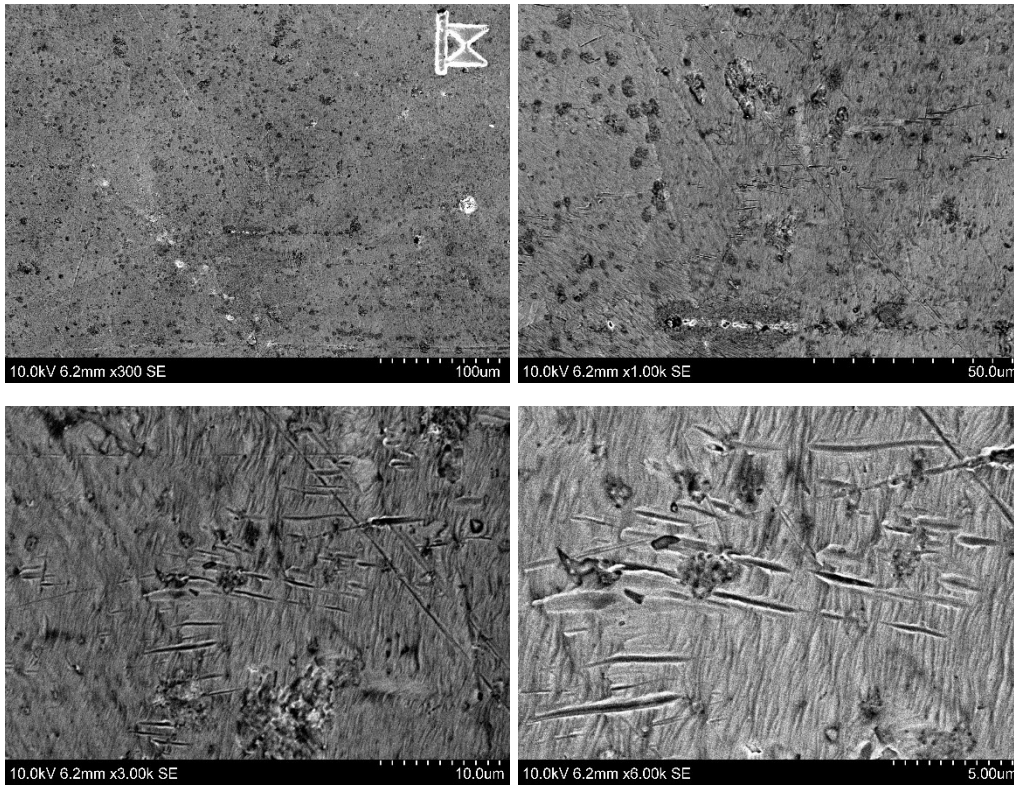
A) Area 1



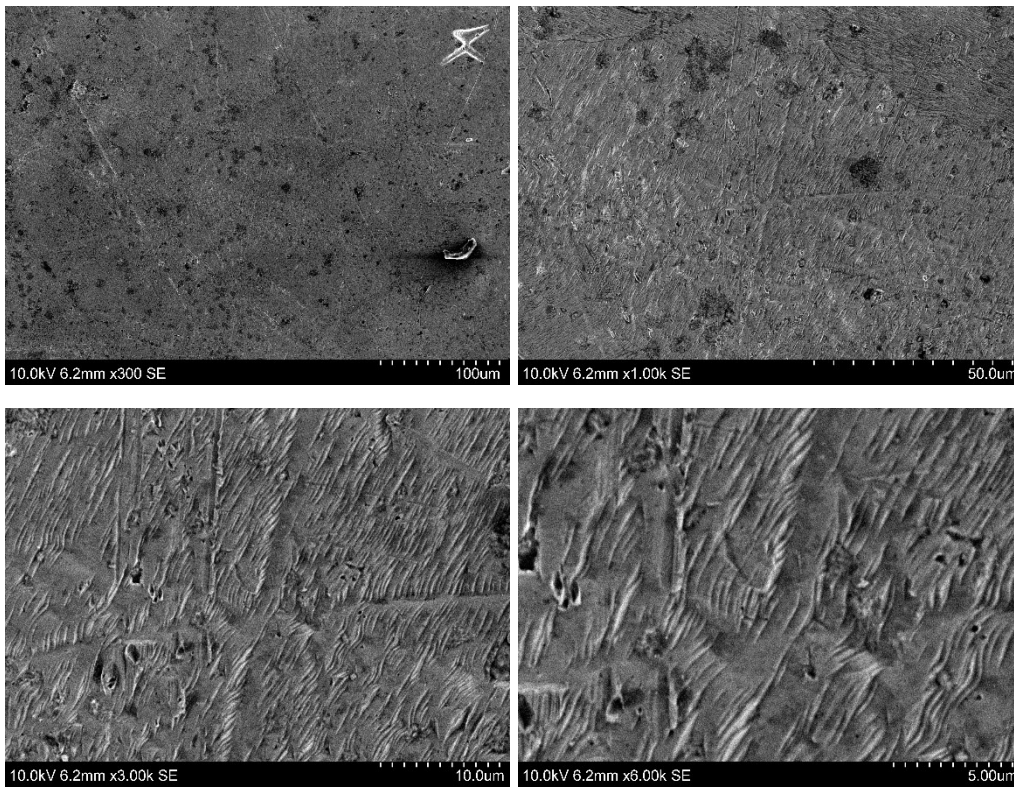
B) Area 2



C) Area 3



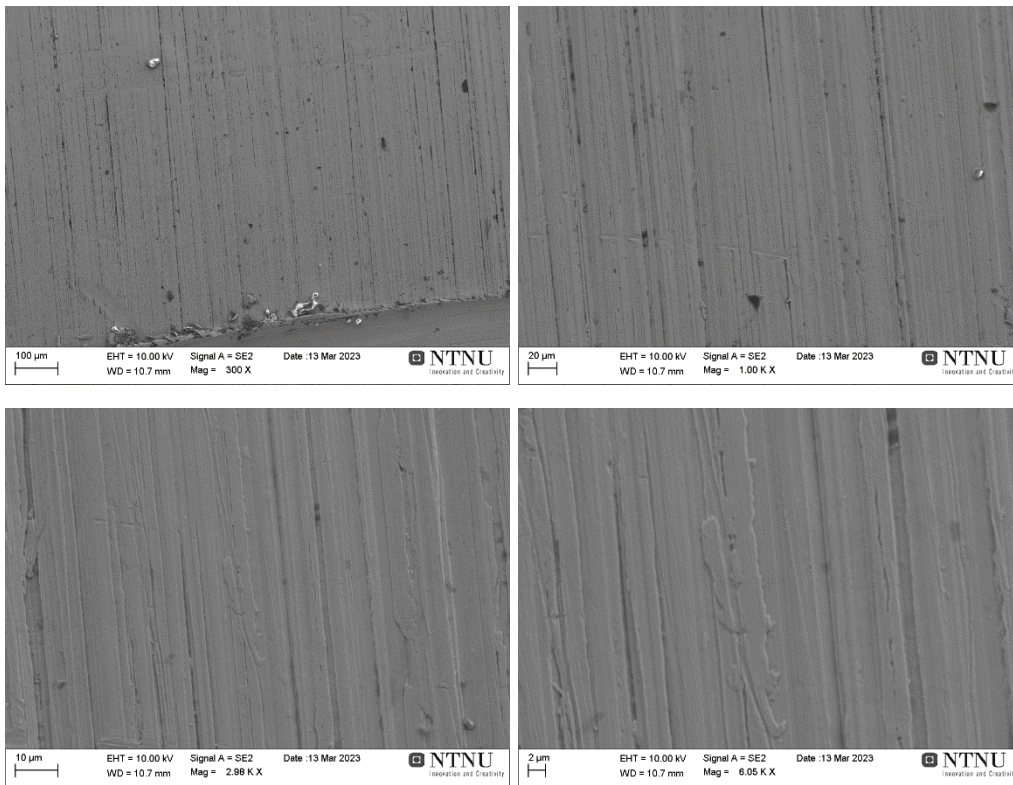
D) Area 4



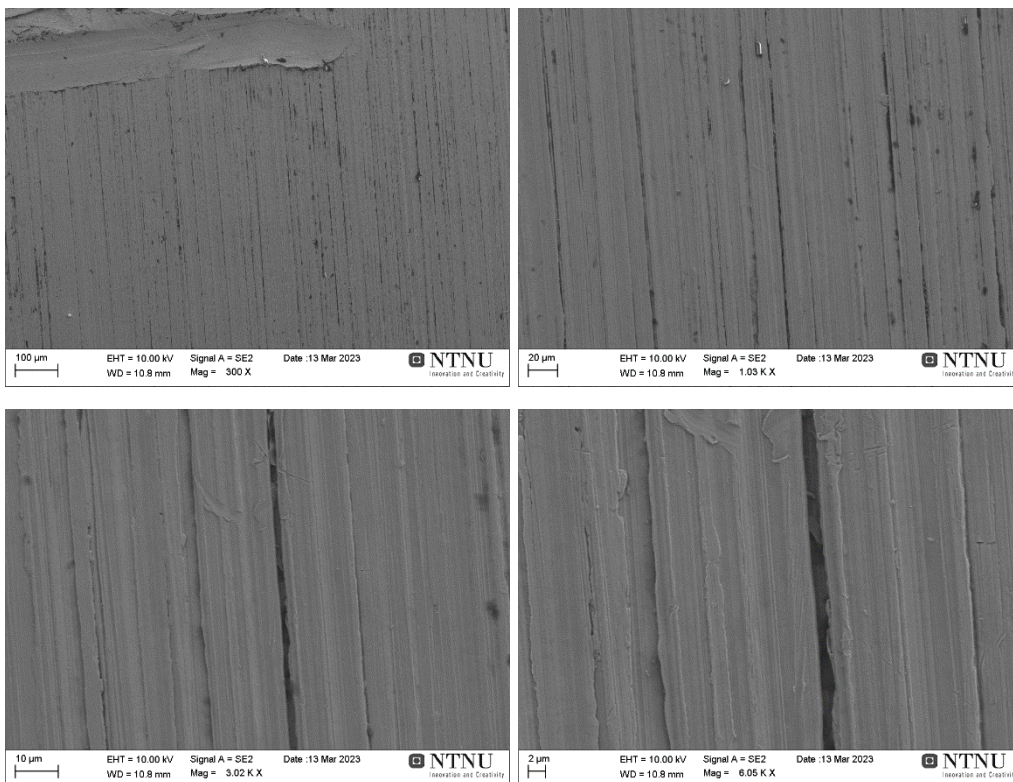


# Appendix B – Syngas oxidation experiments

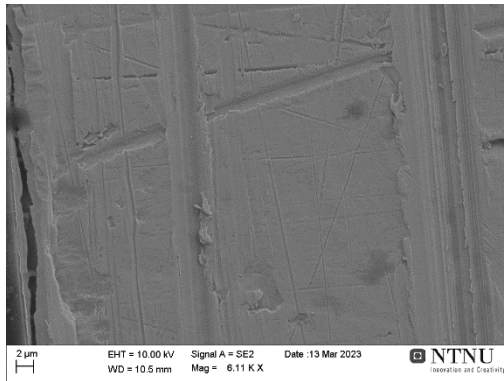
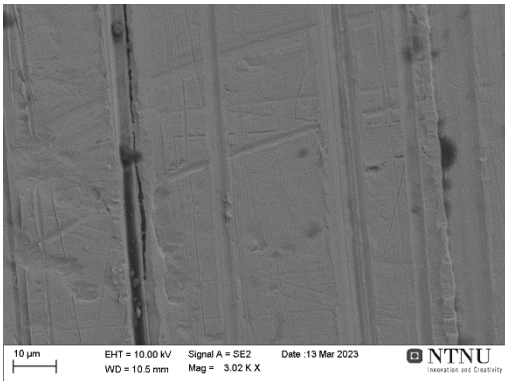
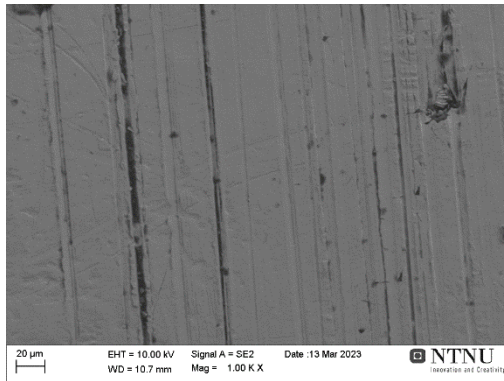
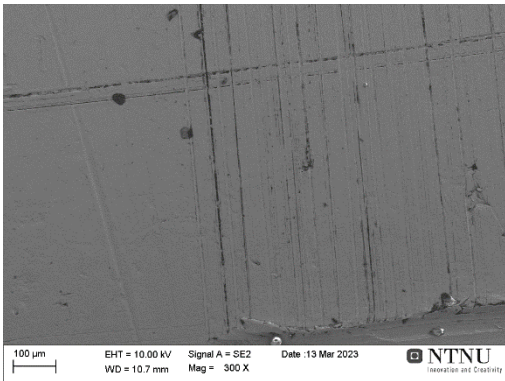
1. Fresh images of the catalyst  
A) Area 1



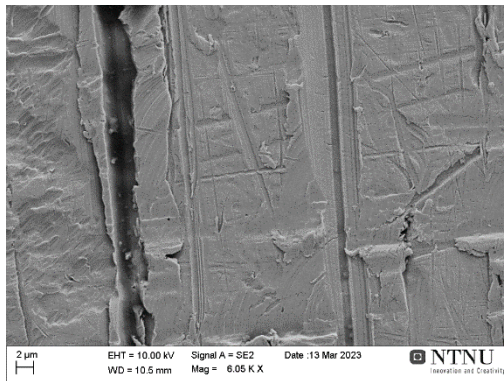
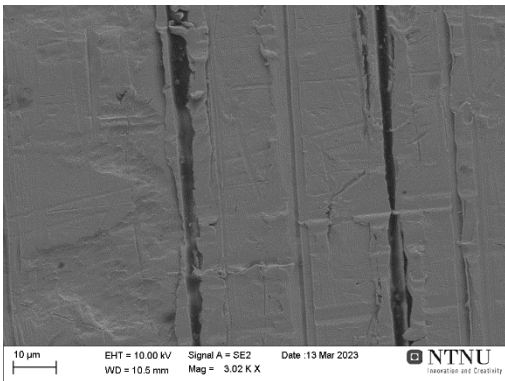
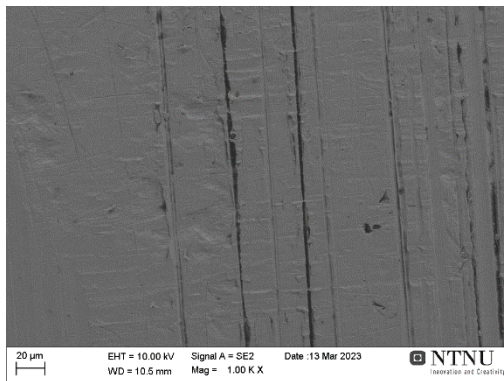
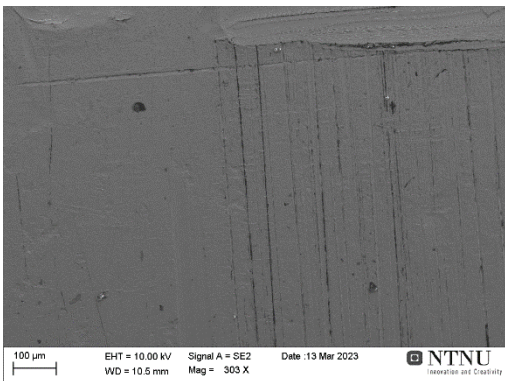
- B) Area 2



### C) Area 3



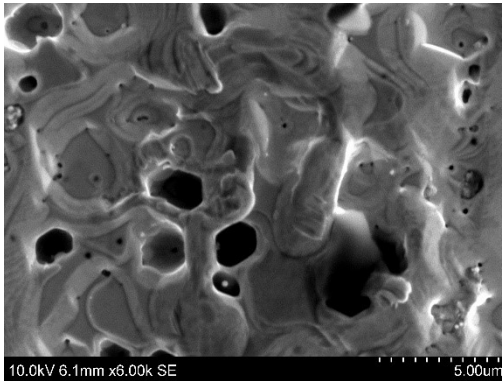
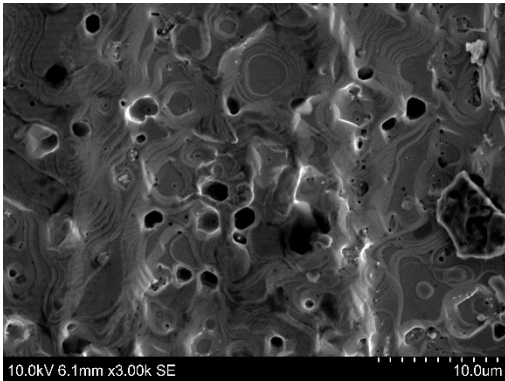
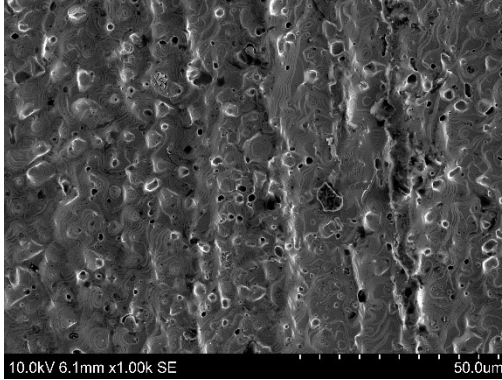
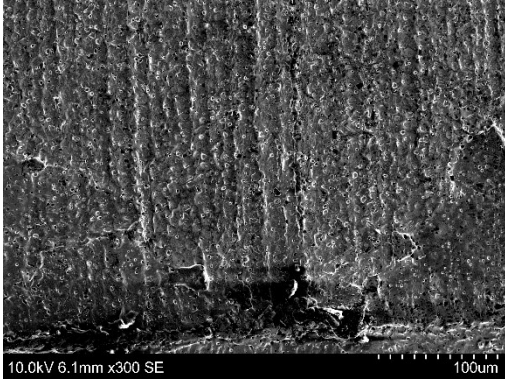
### D) Area 4



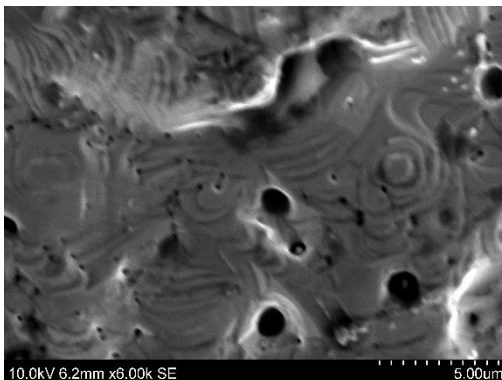
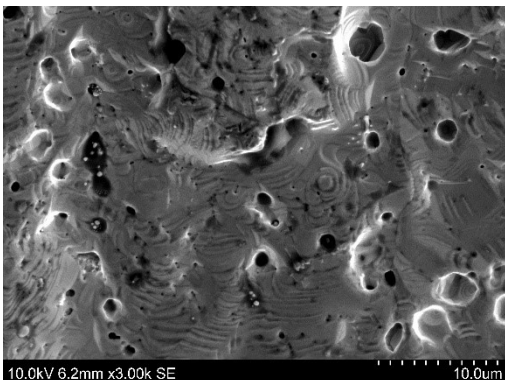
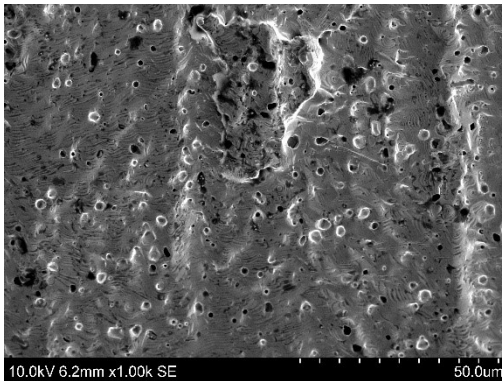
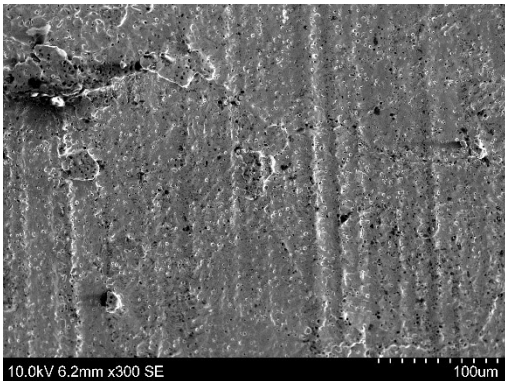


2. 12h experiment catalyst images

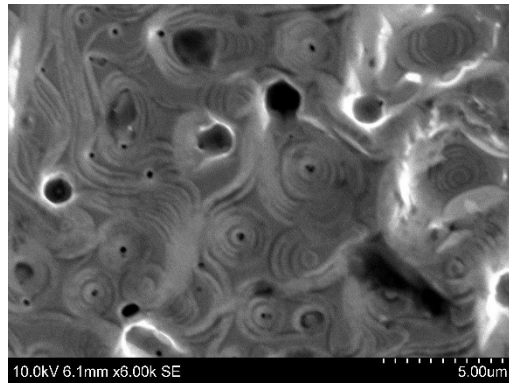
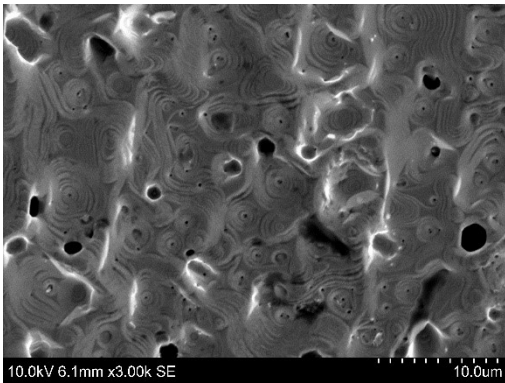
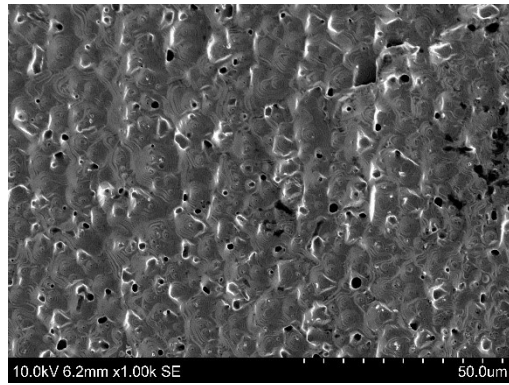
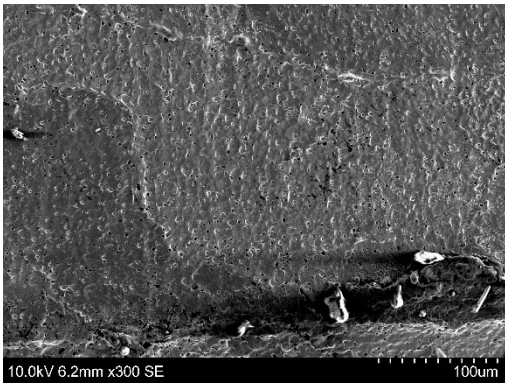
A) Area 1



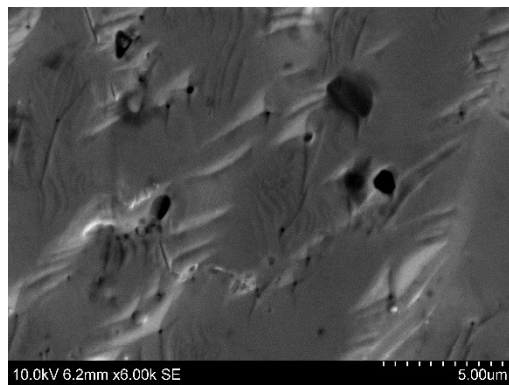
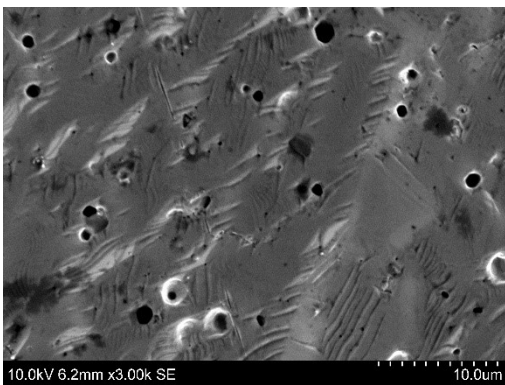
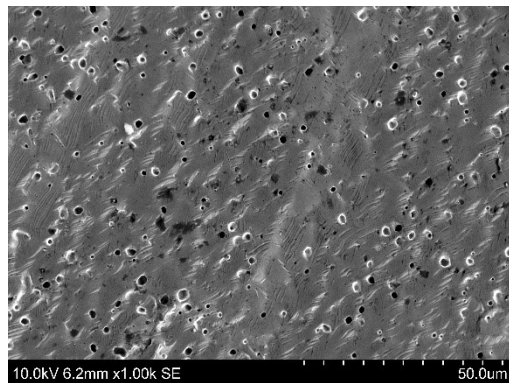
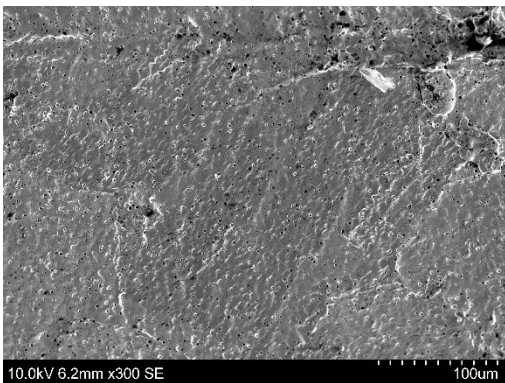
B) Area 2



C) Area 3

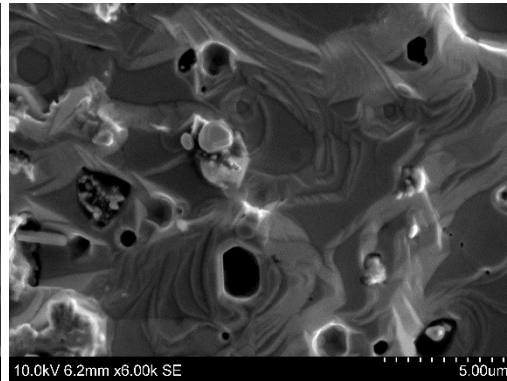
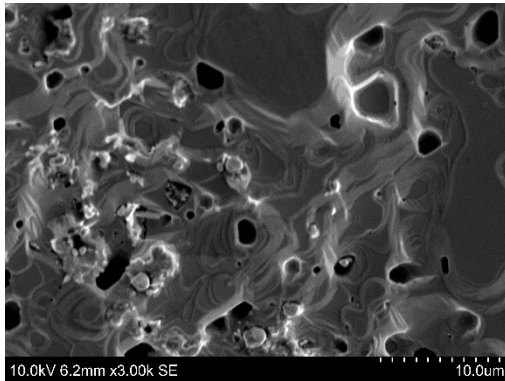
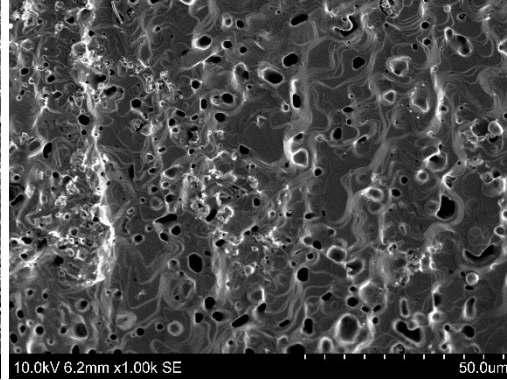
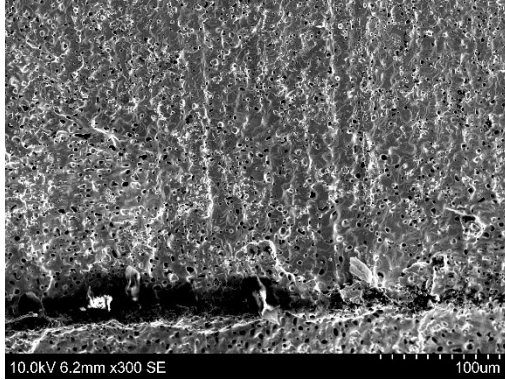


D) Area 4

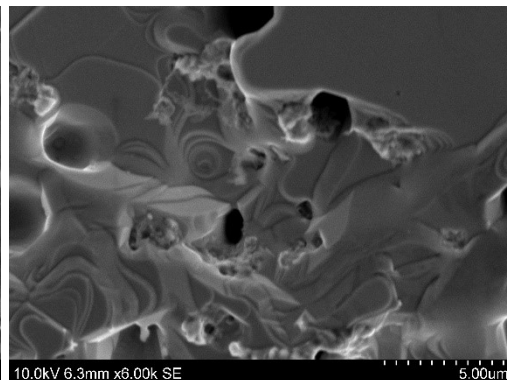
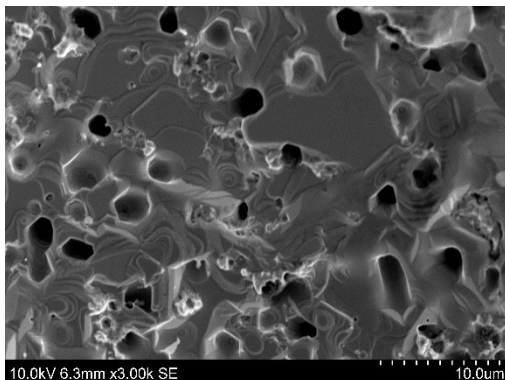
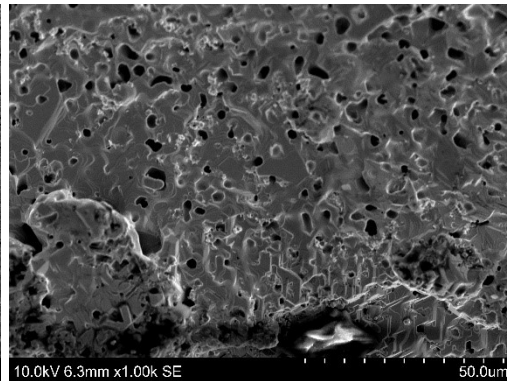
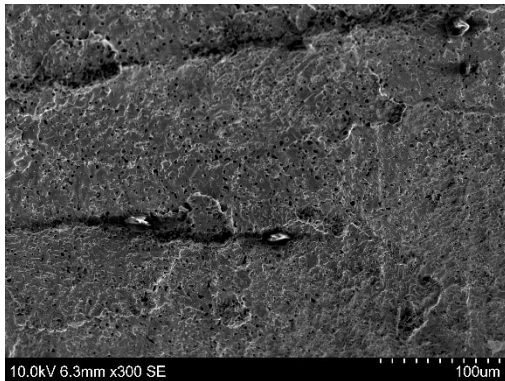


3. 36h experiment images of catalyst

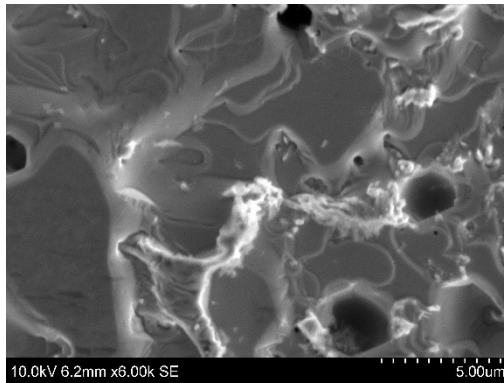
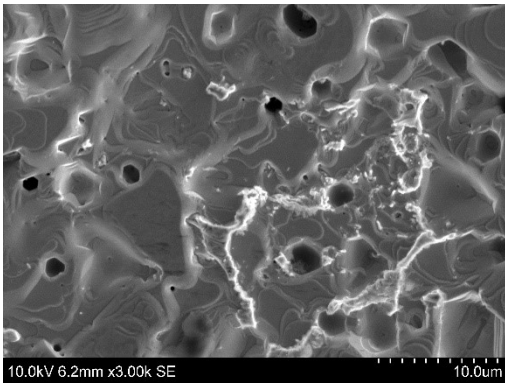
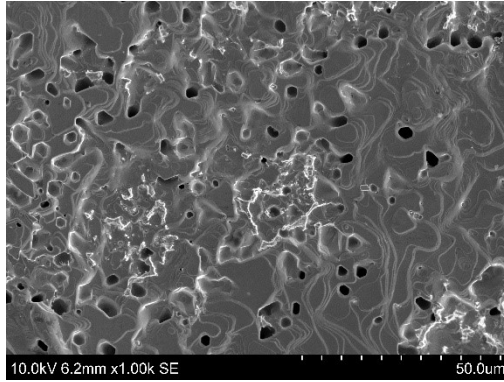
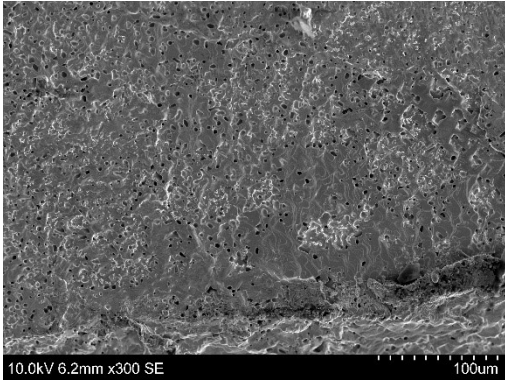
A) Area 1



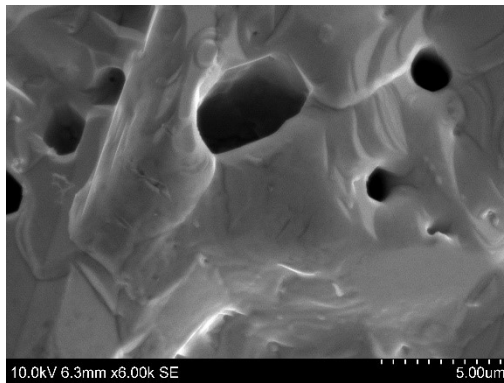
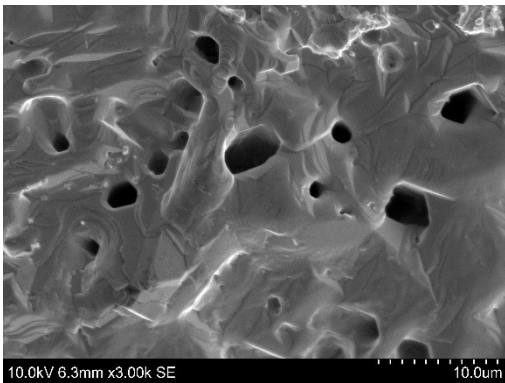
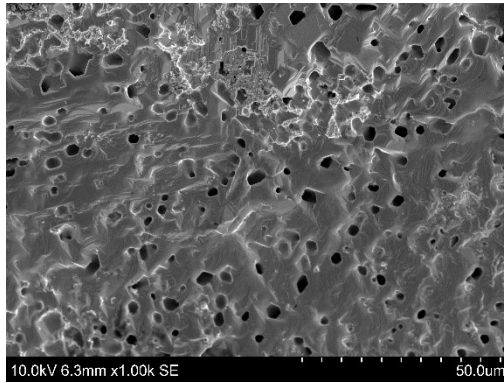
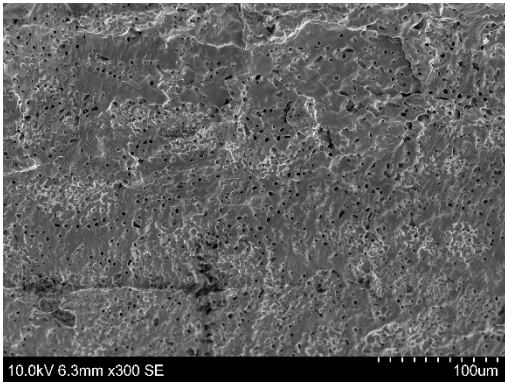
B) Area 2



C) Area 3

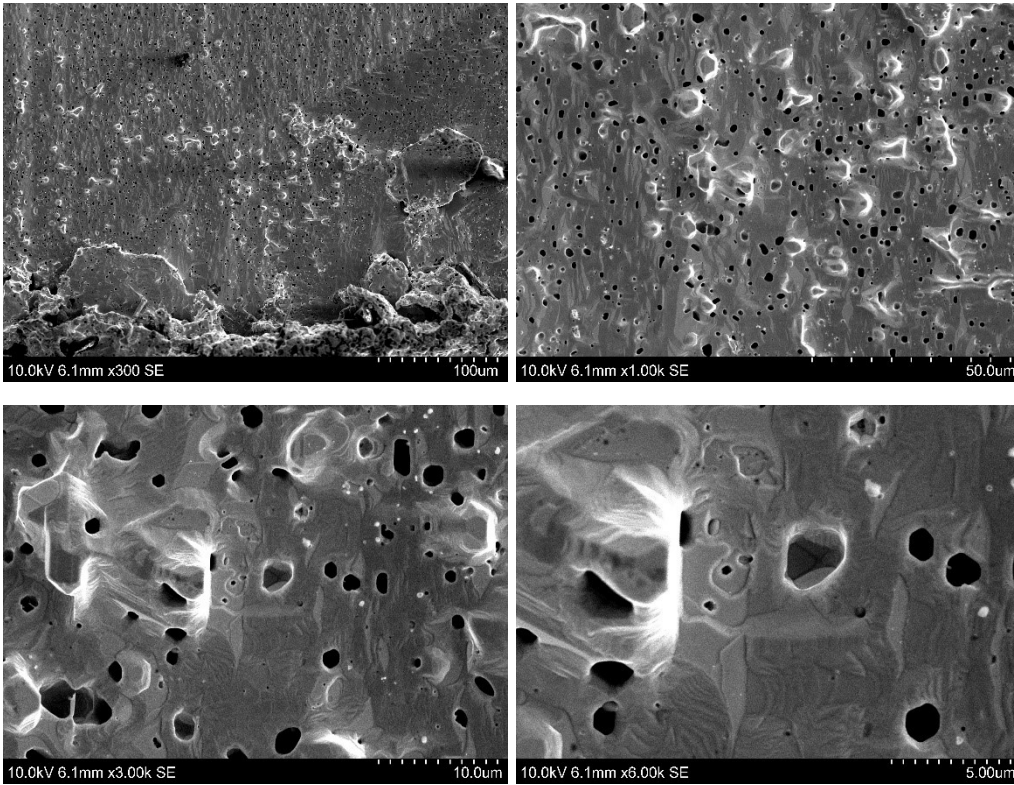


D) Area 4

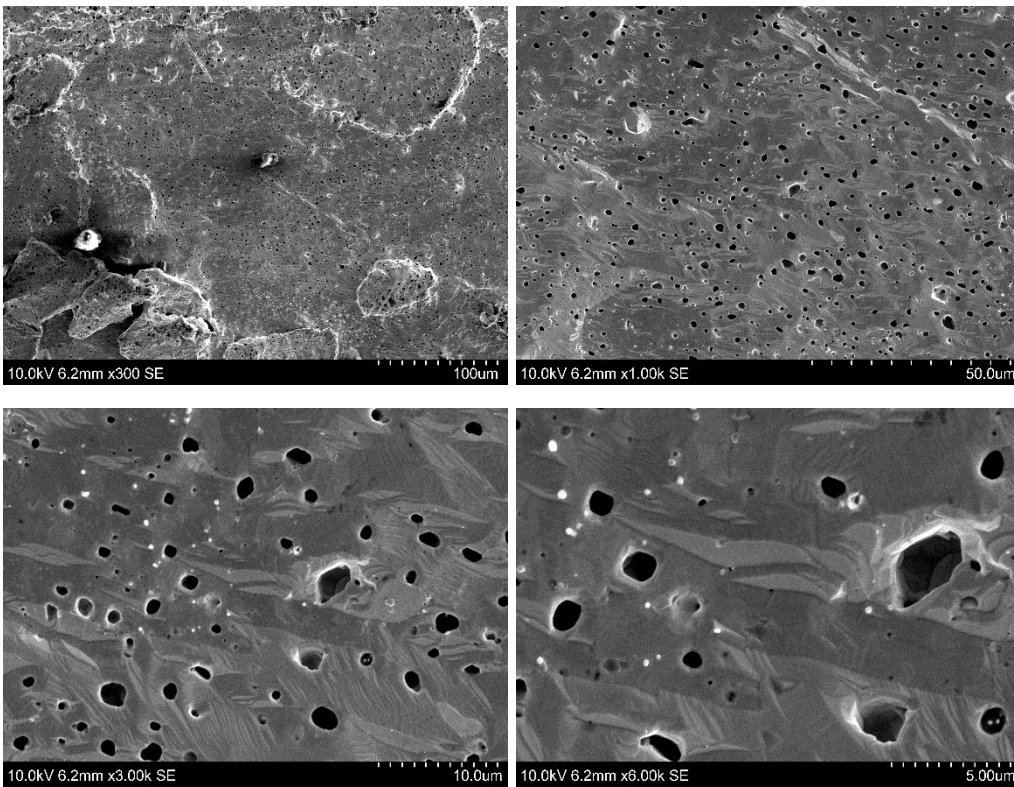




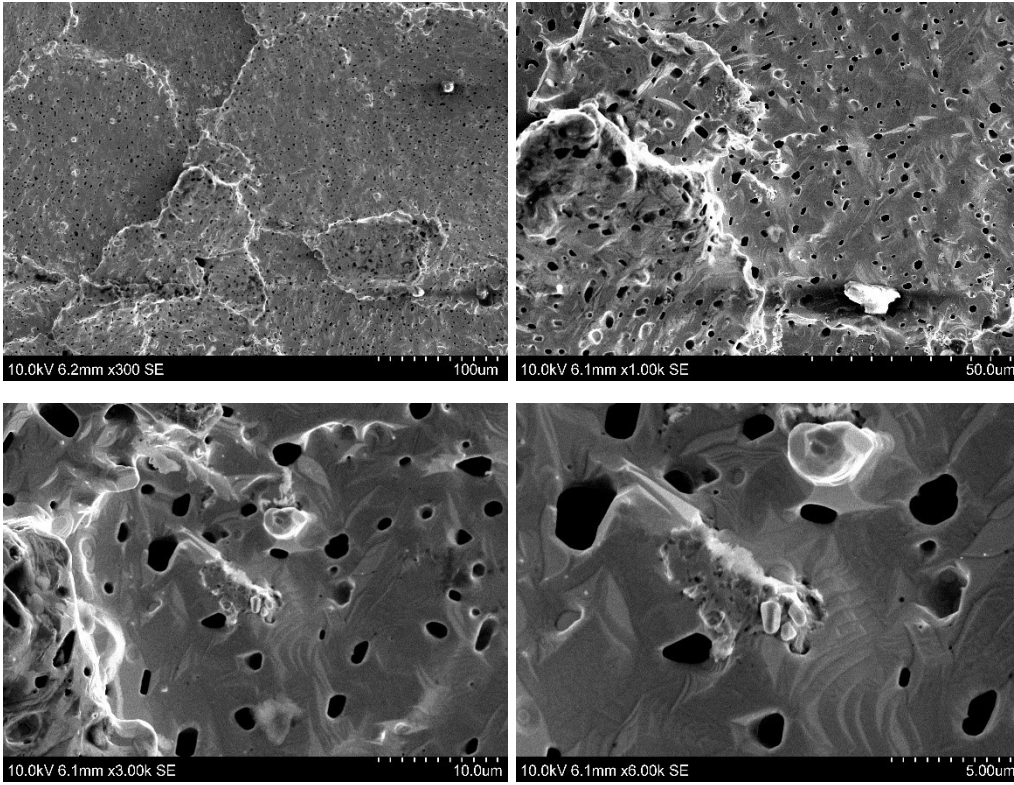
4. 84h experiment images of the catalyst  
A) Area 1



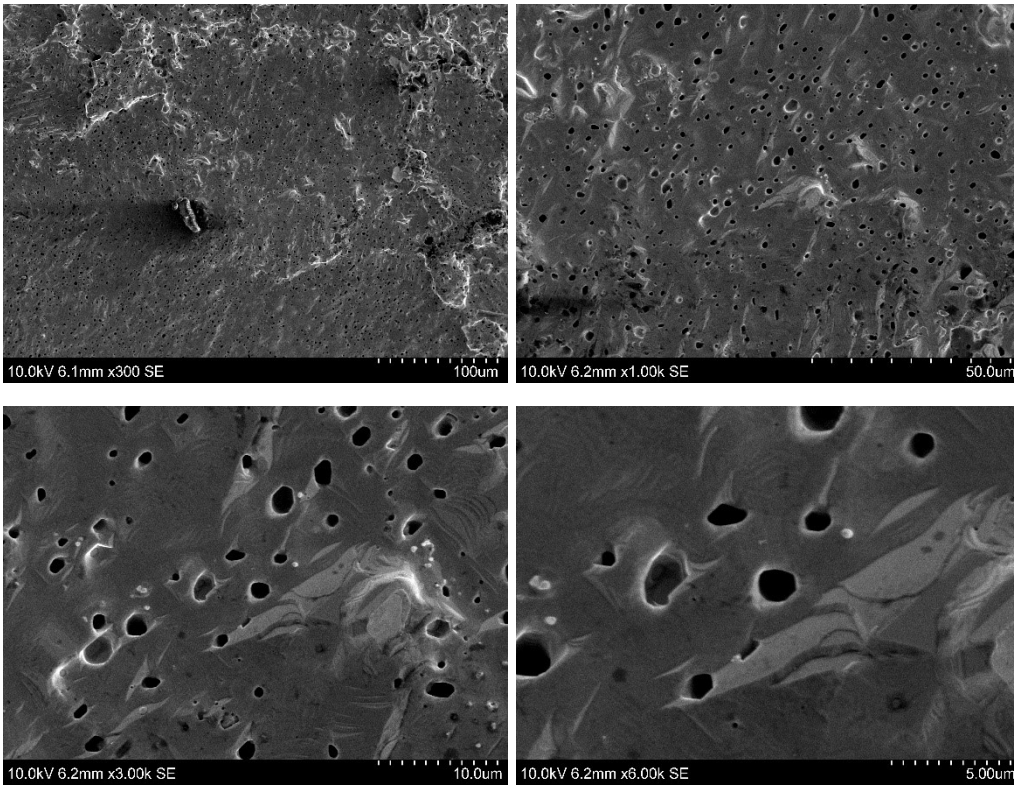
B) Area 2



C) Area 3



D) Area 4

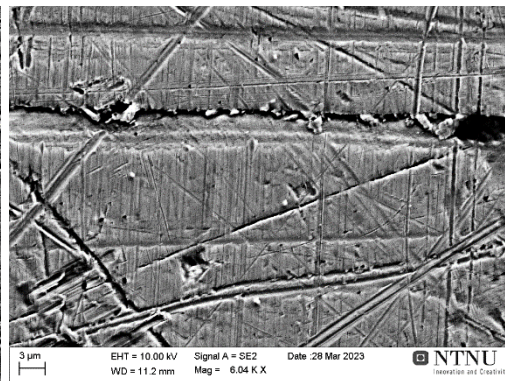
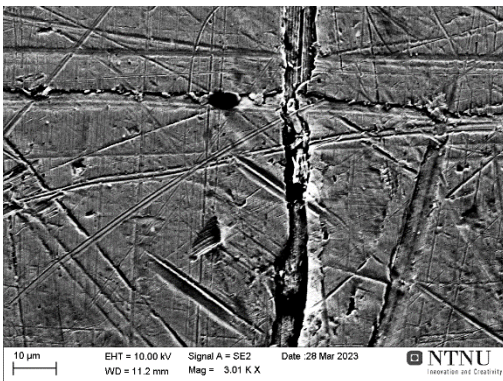
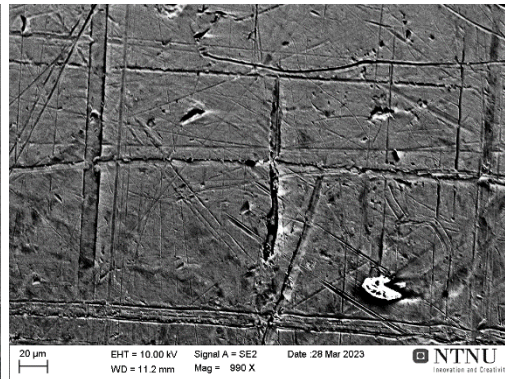
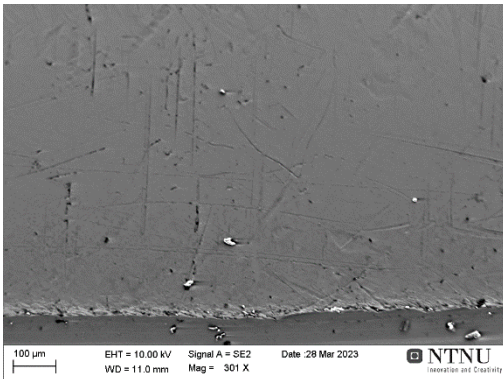




# Appendix C – CO oxidation with water vapour experiment

## 1. Fresh catalyst images

### A) Area 1

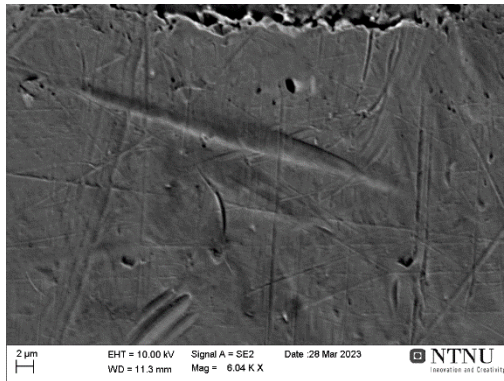
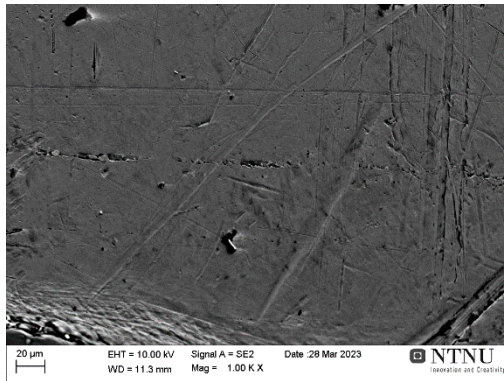
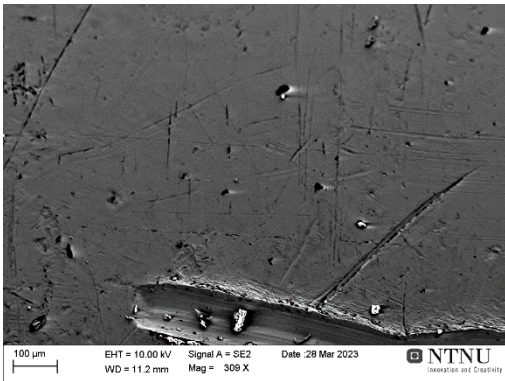


### B) Area 2

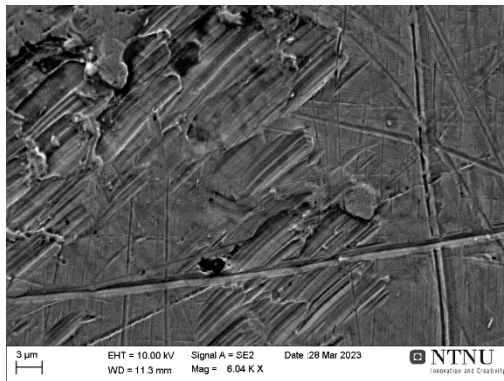
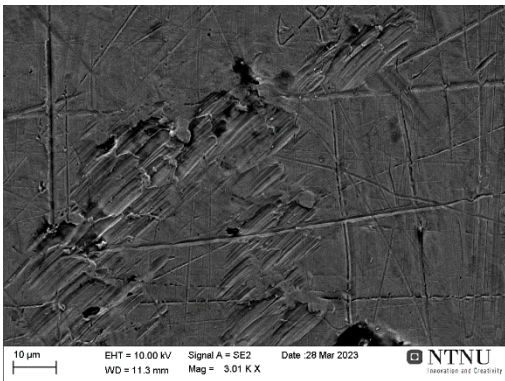
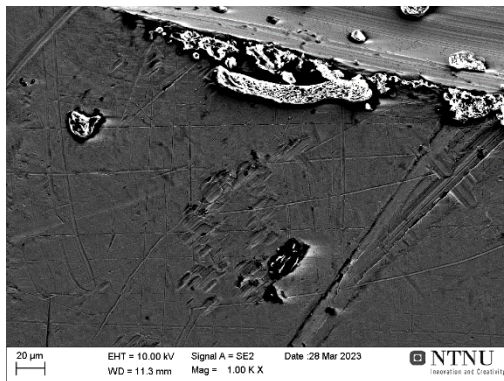
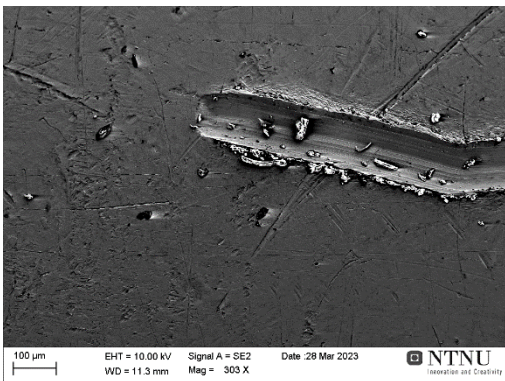




### C) Area 3



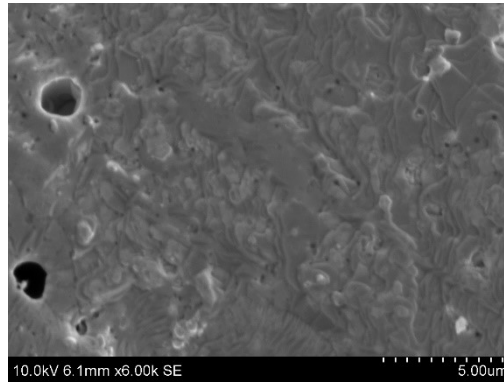
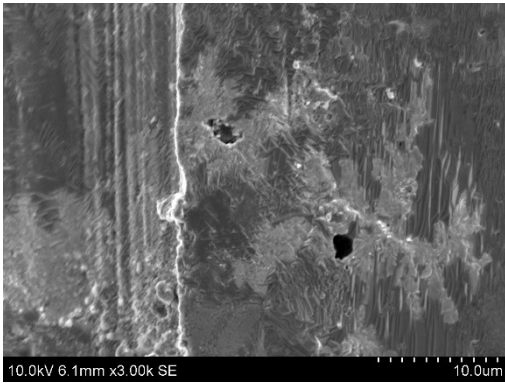
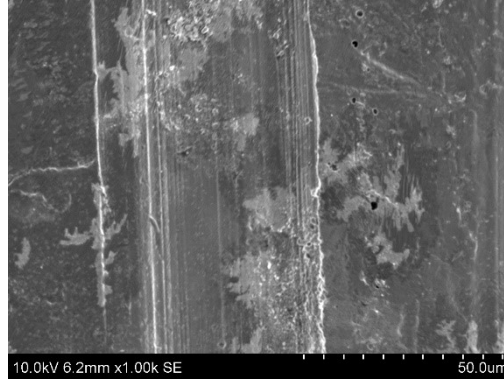
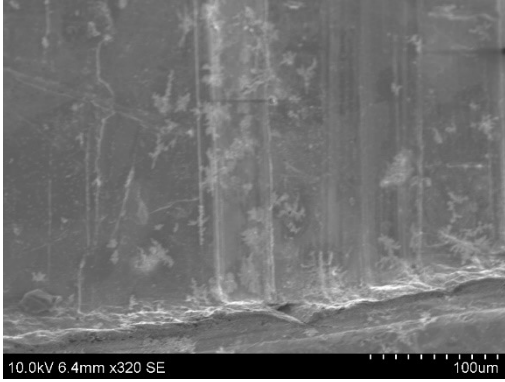
### D) Area 4



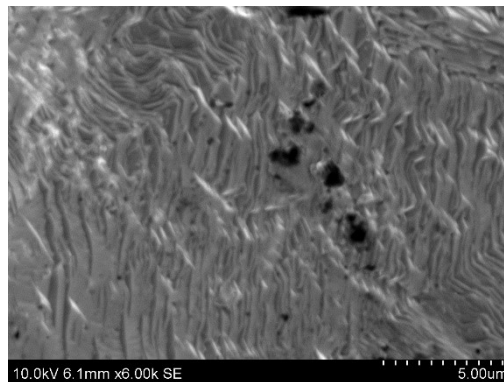
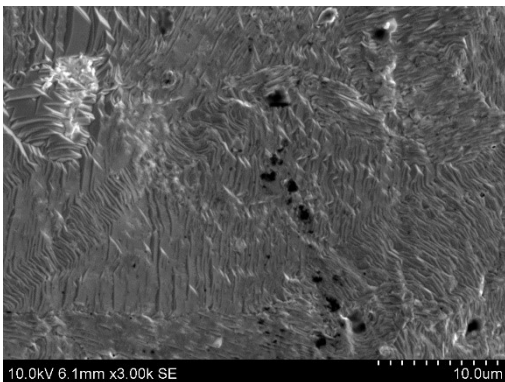
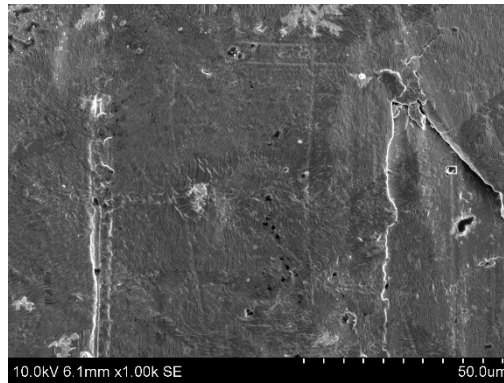
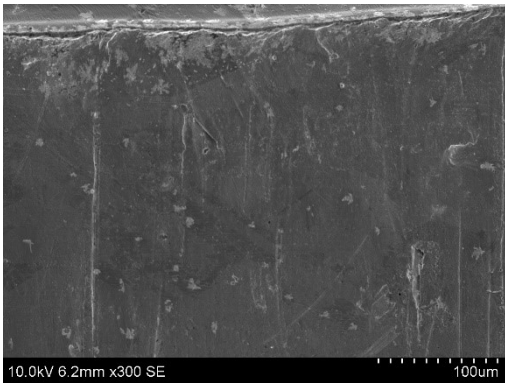


2. 12h experiment catalyst images

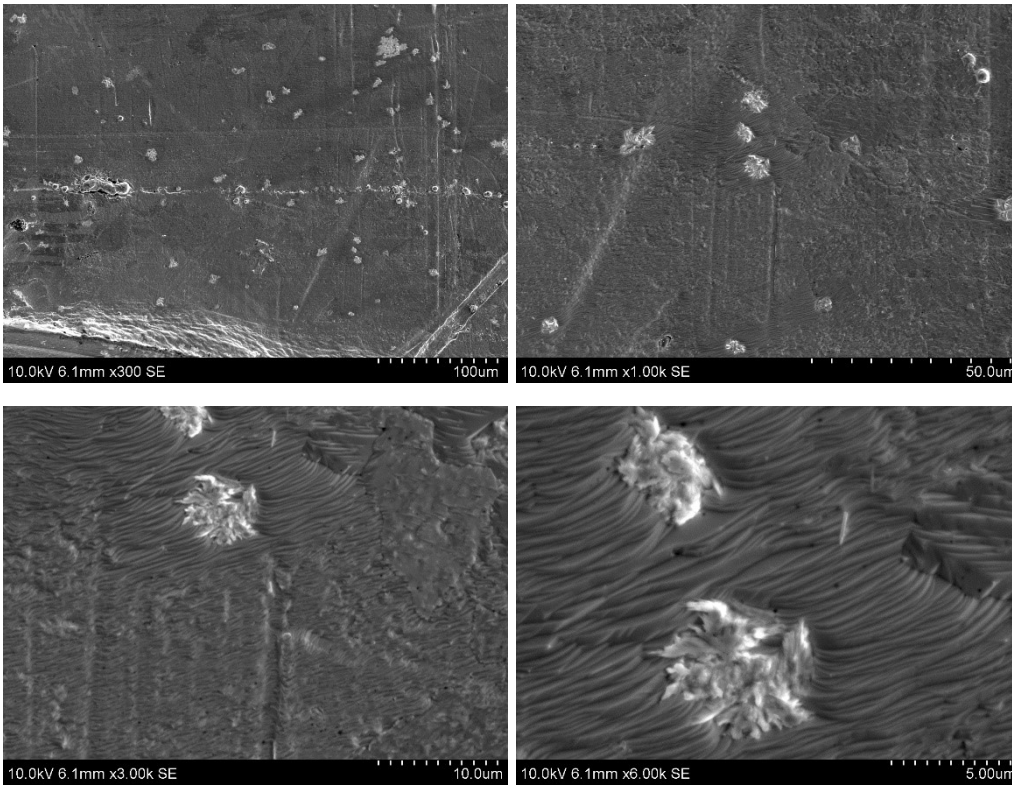
A) Area 1



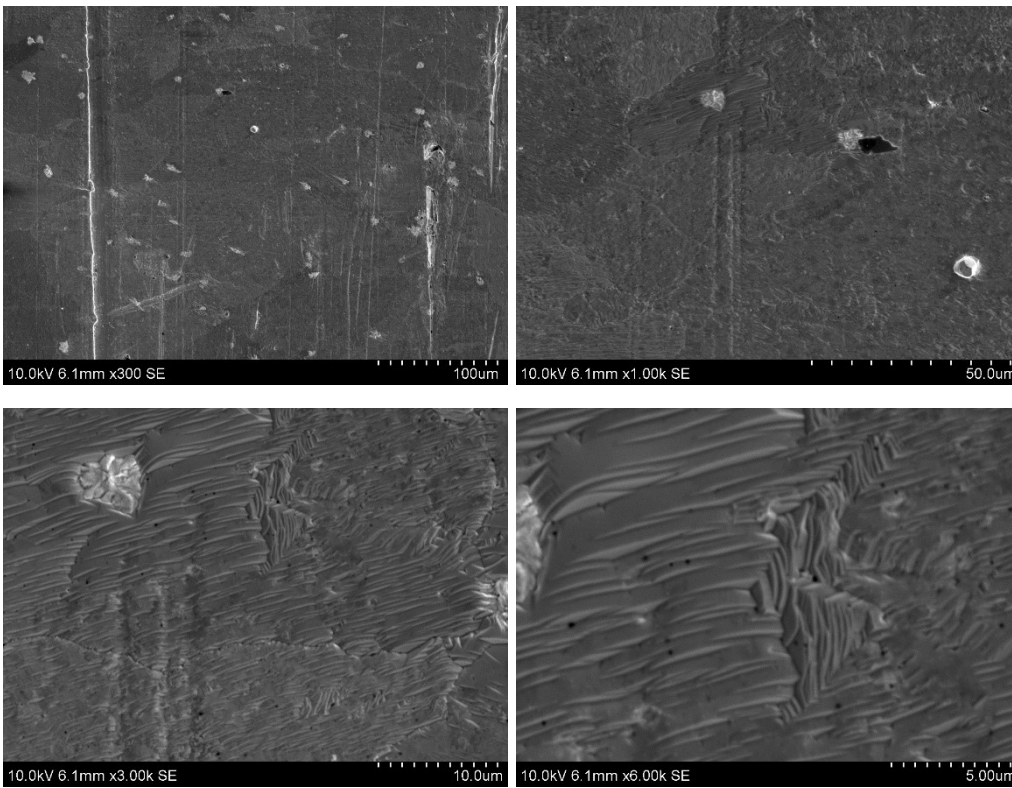
B) Area 2



C) Area 3

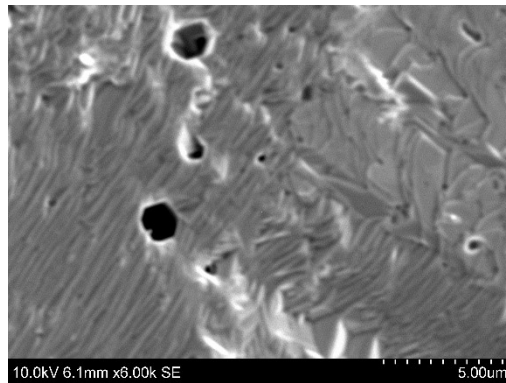
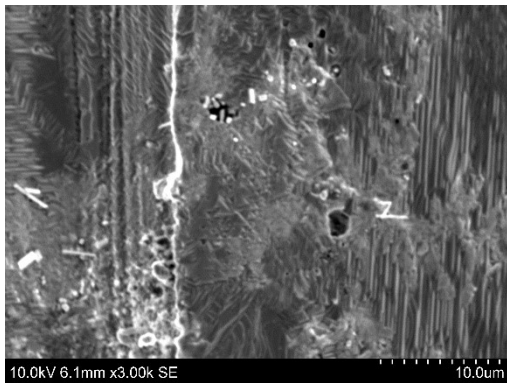
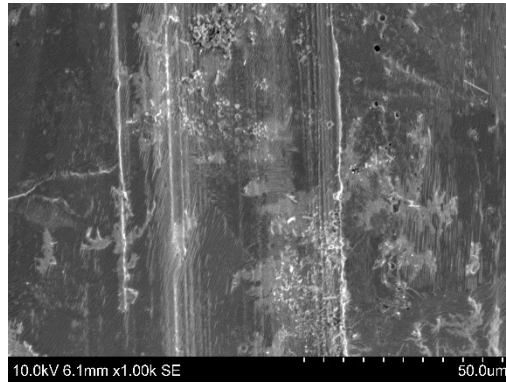
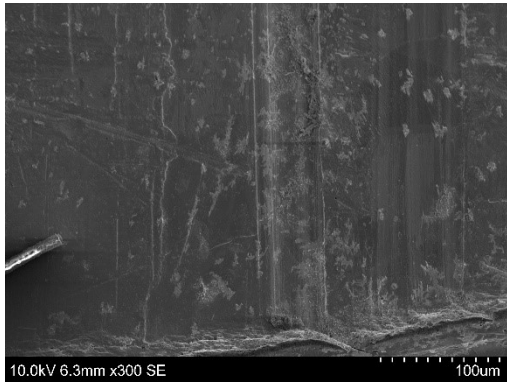


D) Area 4

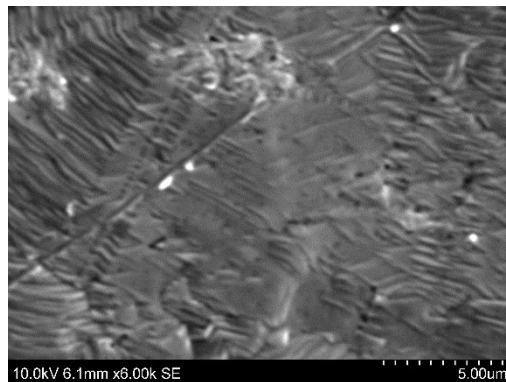
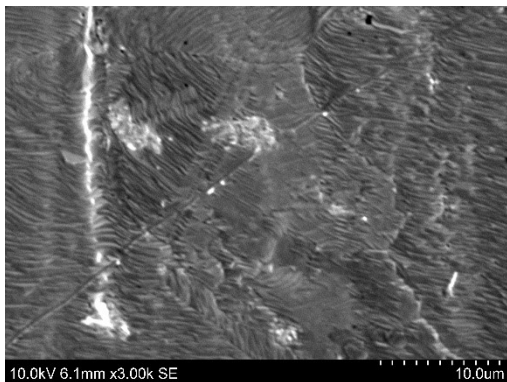
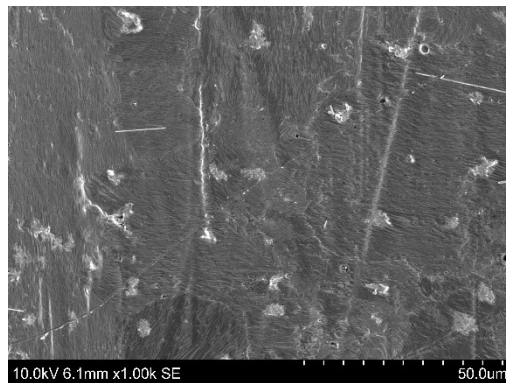
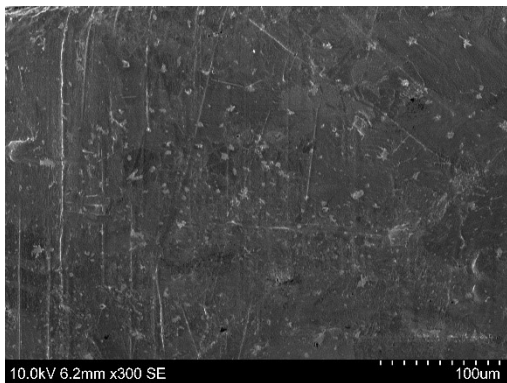


3. 36h experiment catalyst images

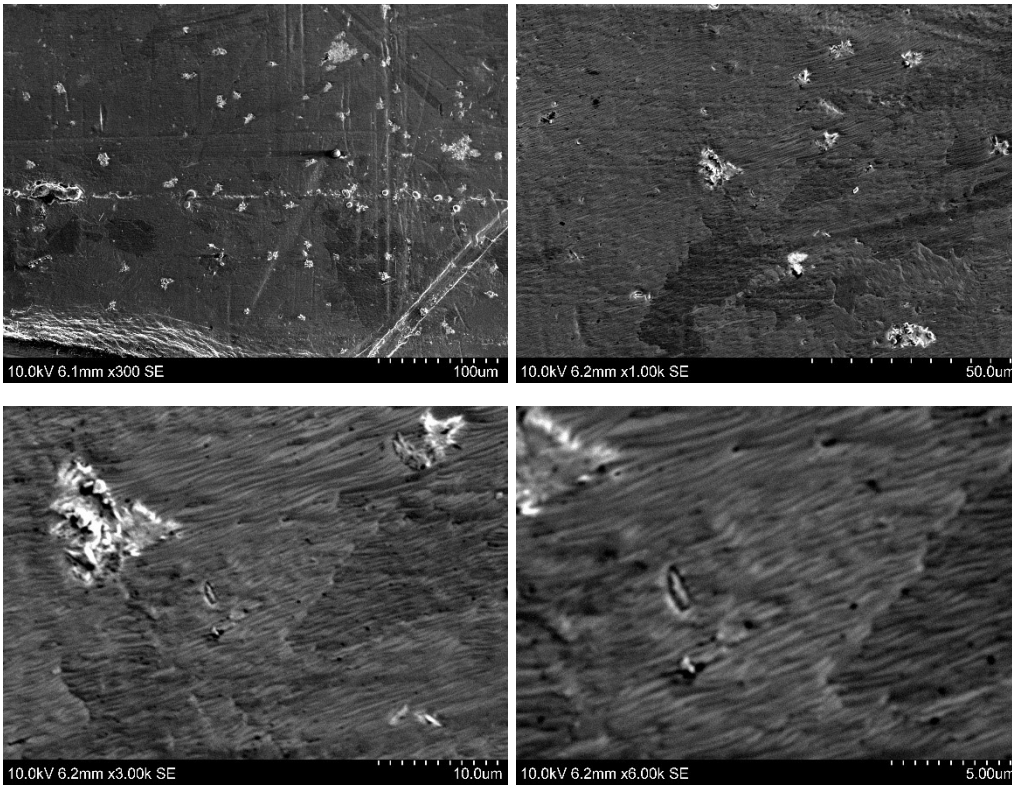
A) Area 1



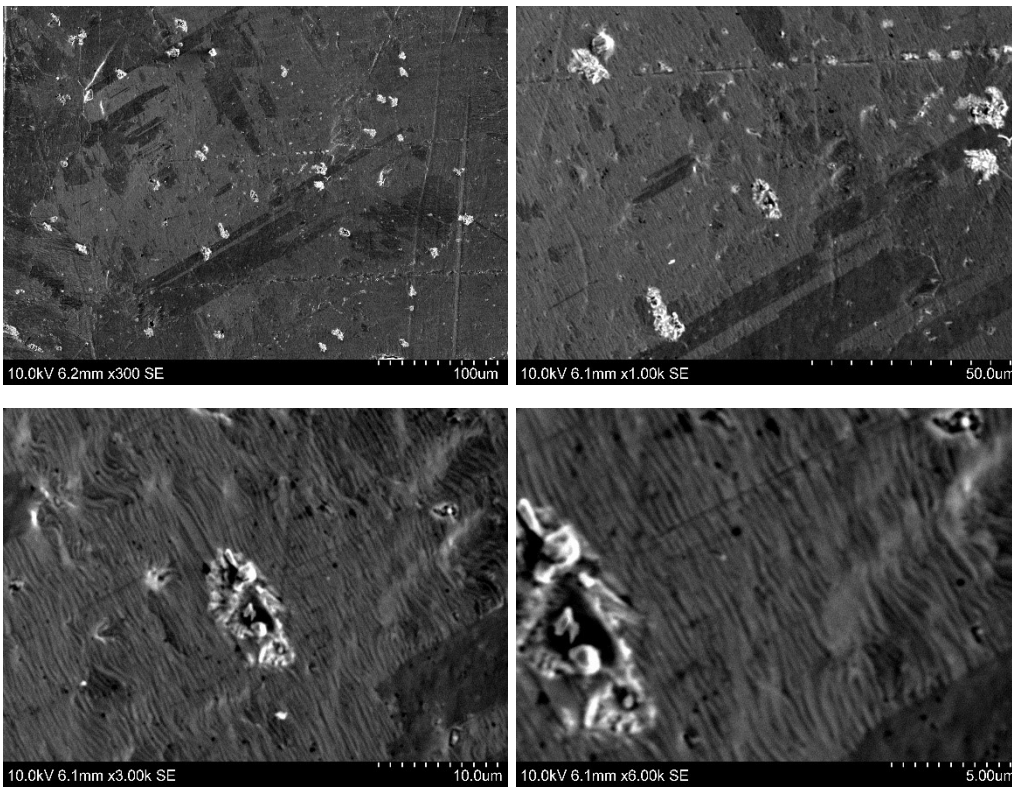
B) Area 2



C) Area 3



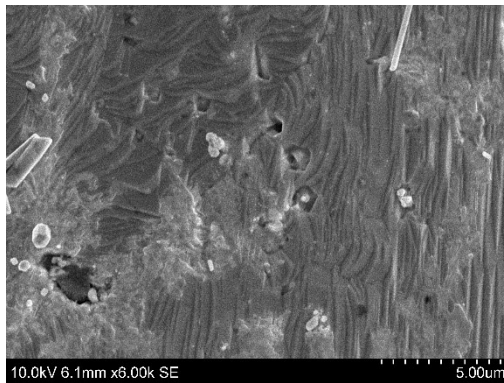
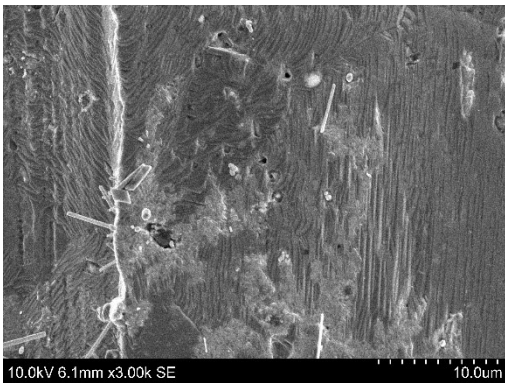
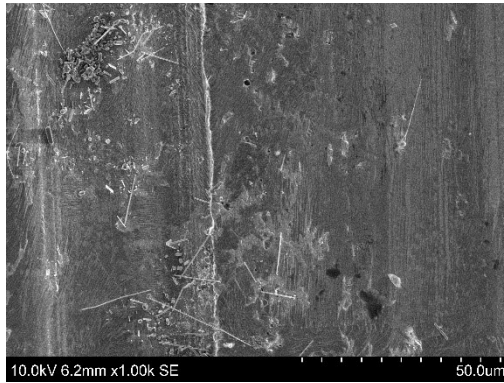
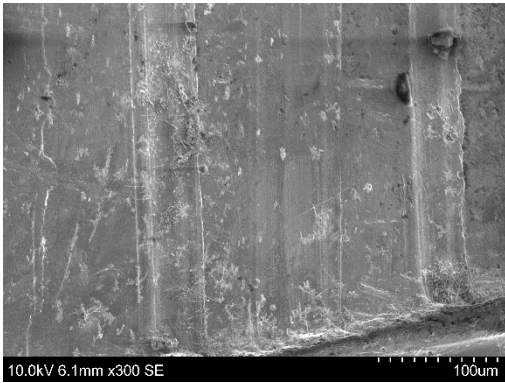
D) Area 4



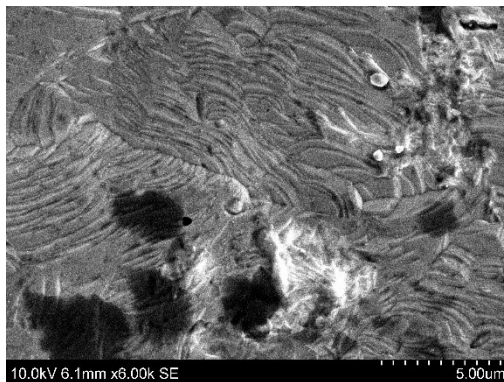
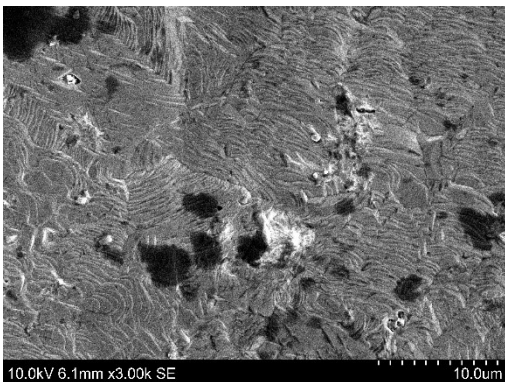
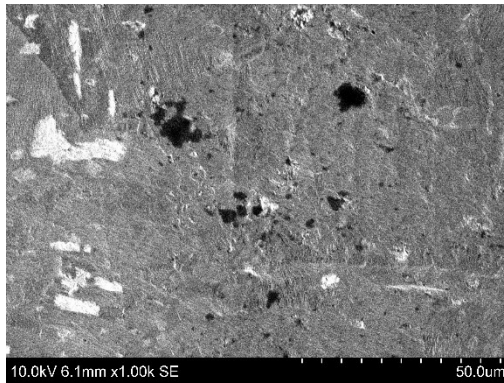
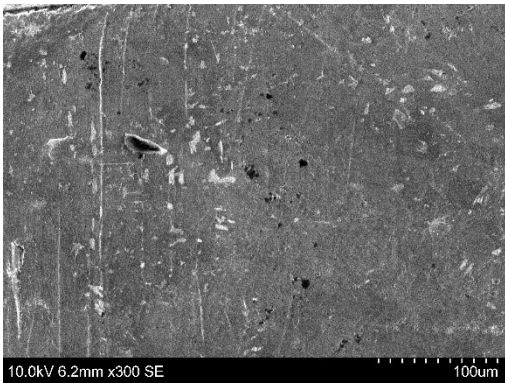


4. 84h experiment catalyst images

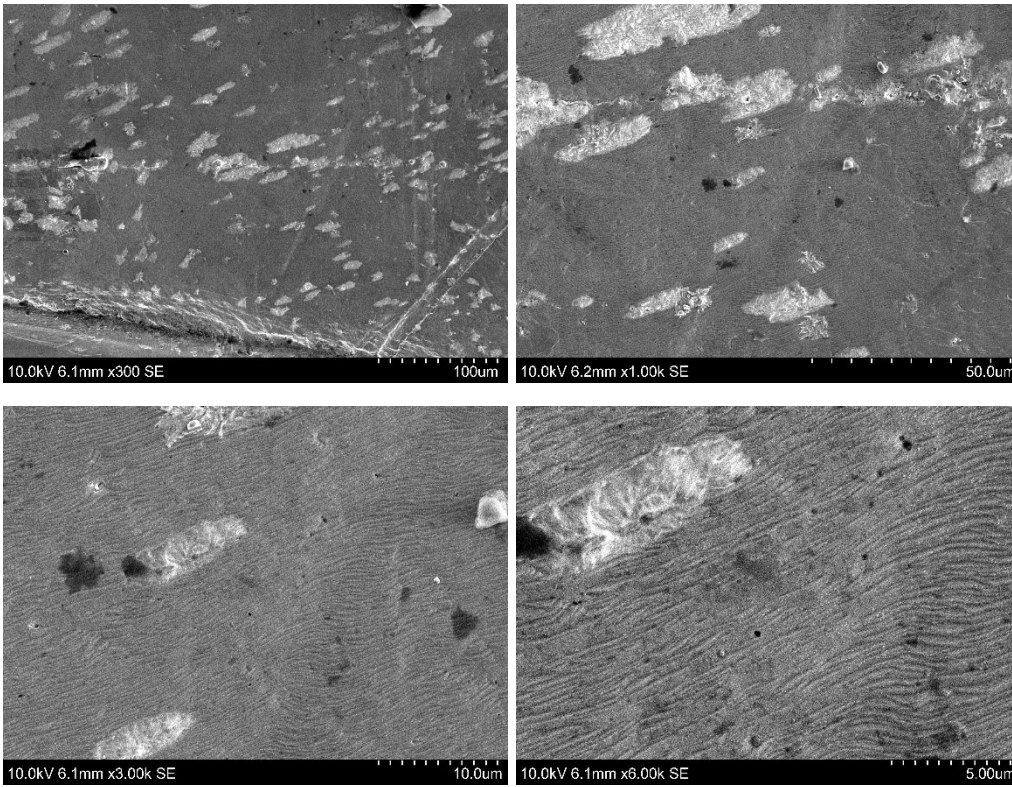
A) Area 1



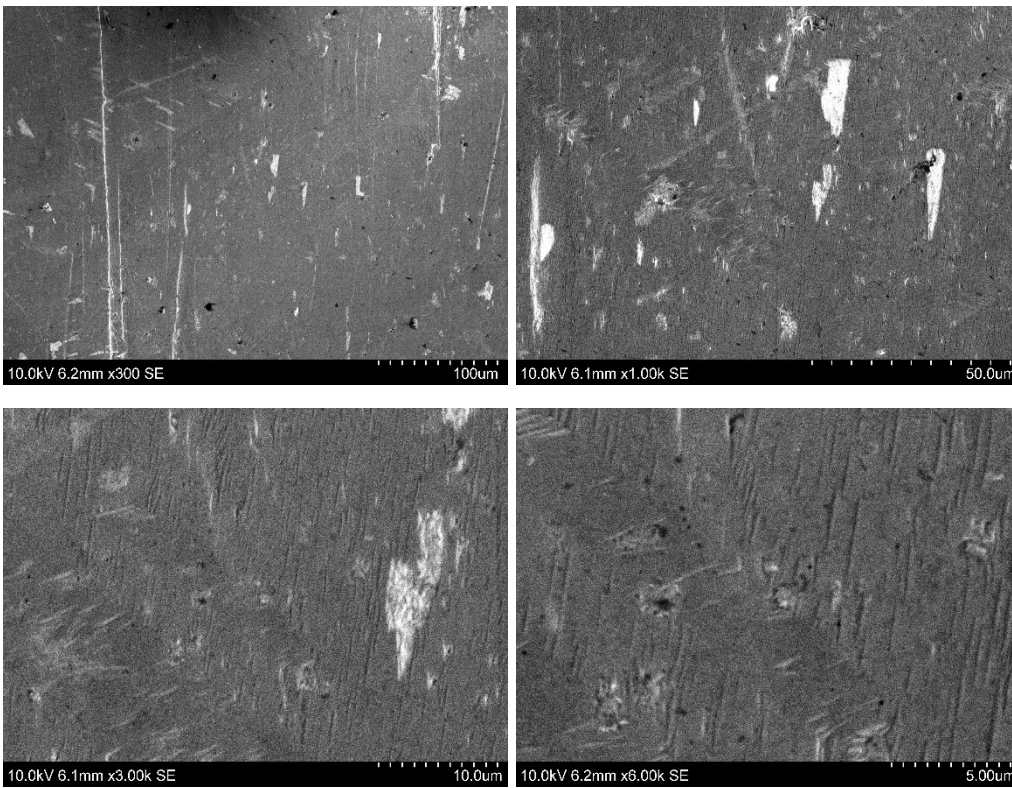
B) Area 2



C) Area 3



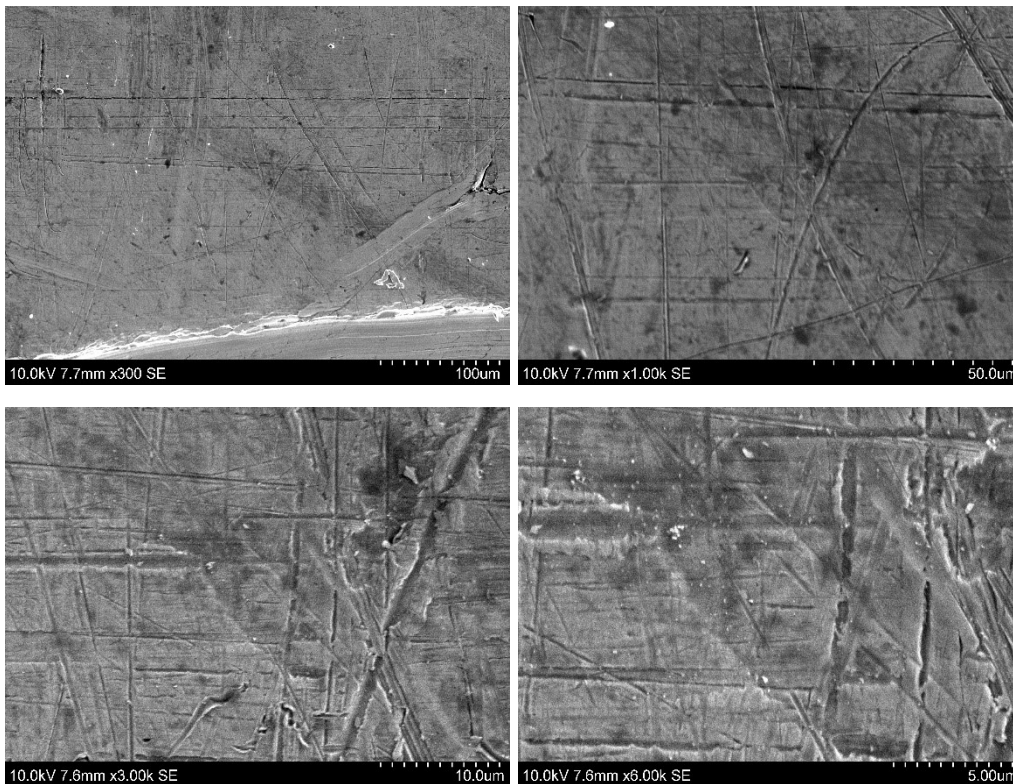
D) Area 4



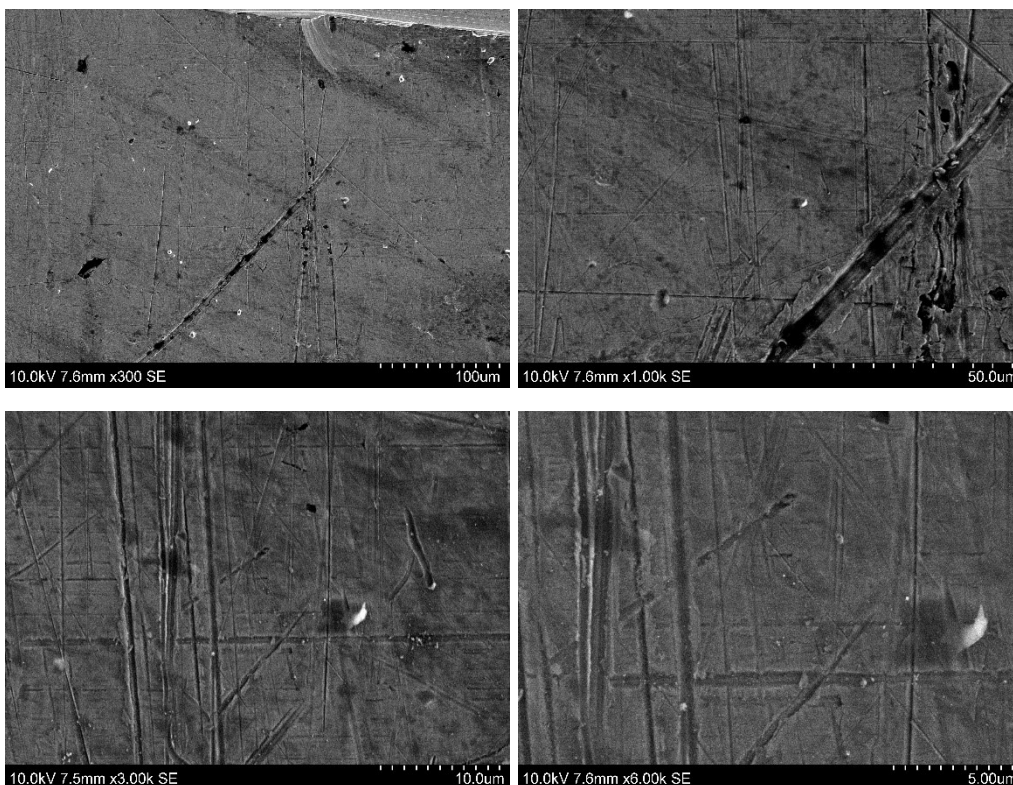
## Appendix D – Hydrogen oxidation with water vapour experiment

### 1. Fresh SEM images of the catalyst

#### A) Area 1

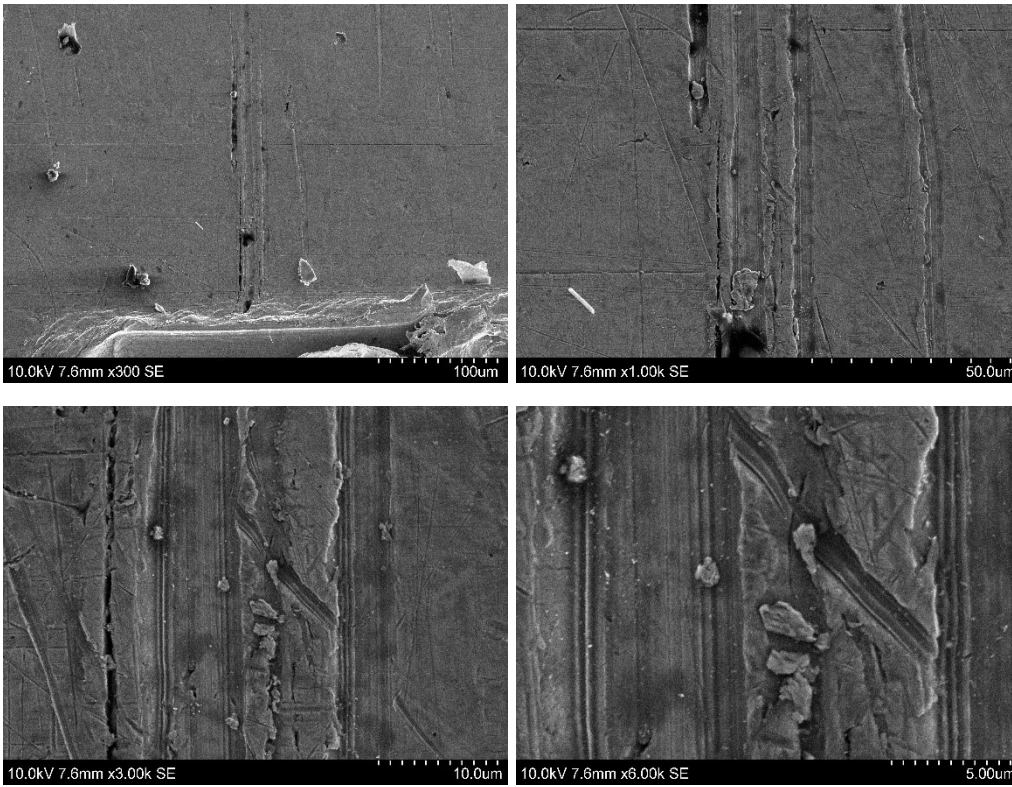


#### B) Area 2

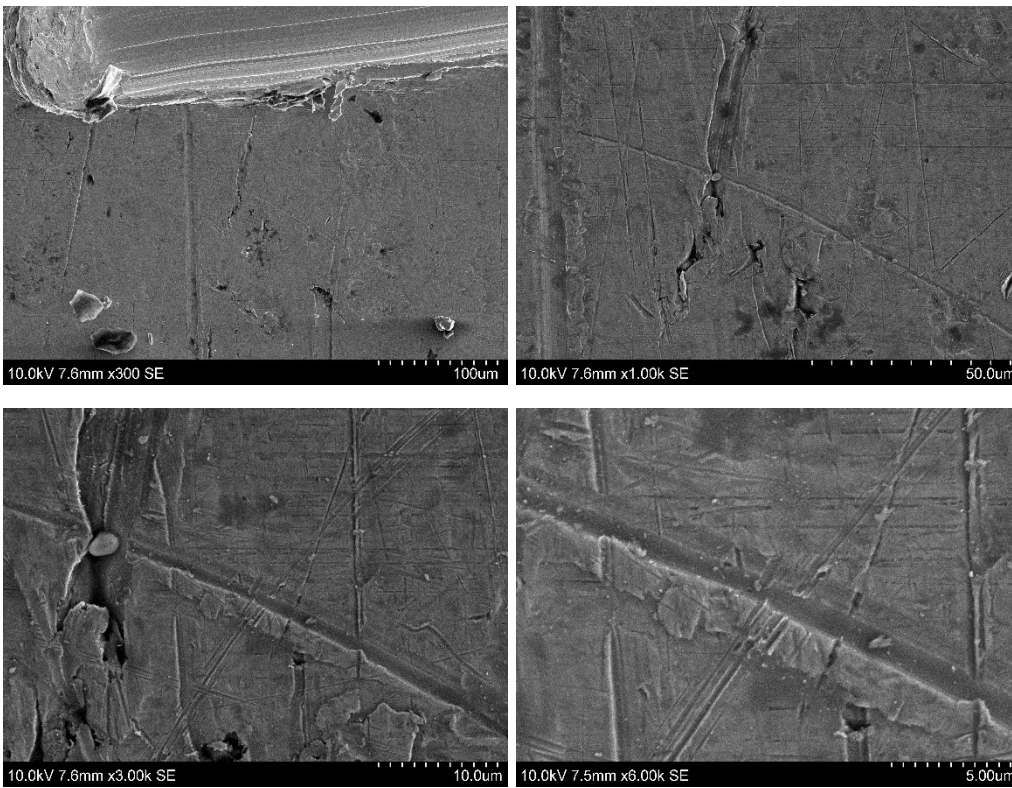




C) Area 3



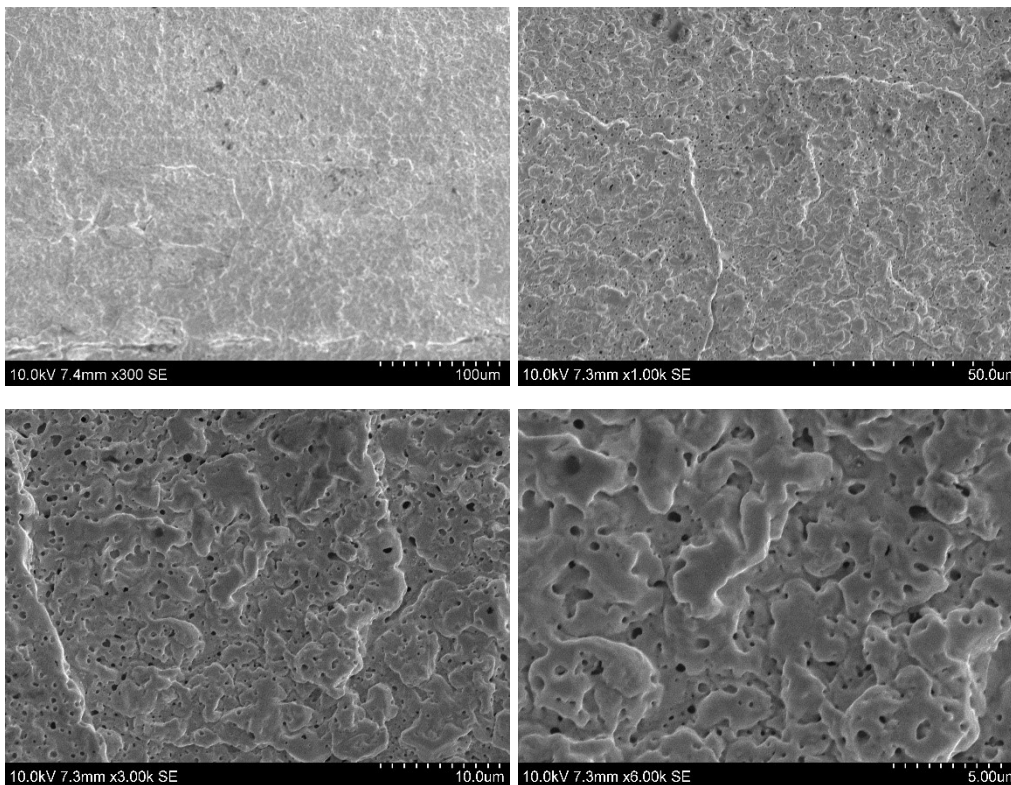
D) Area 4



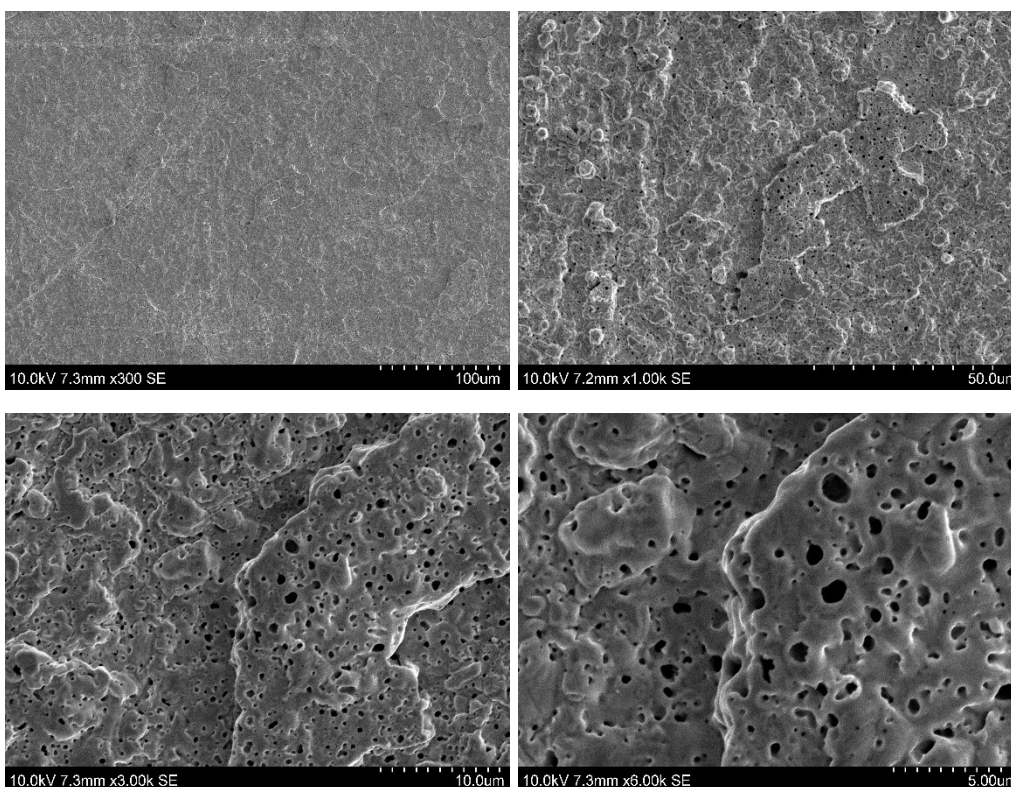


2. 12h experiment catalyst images

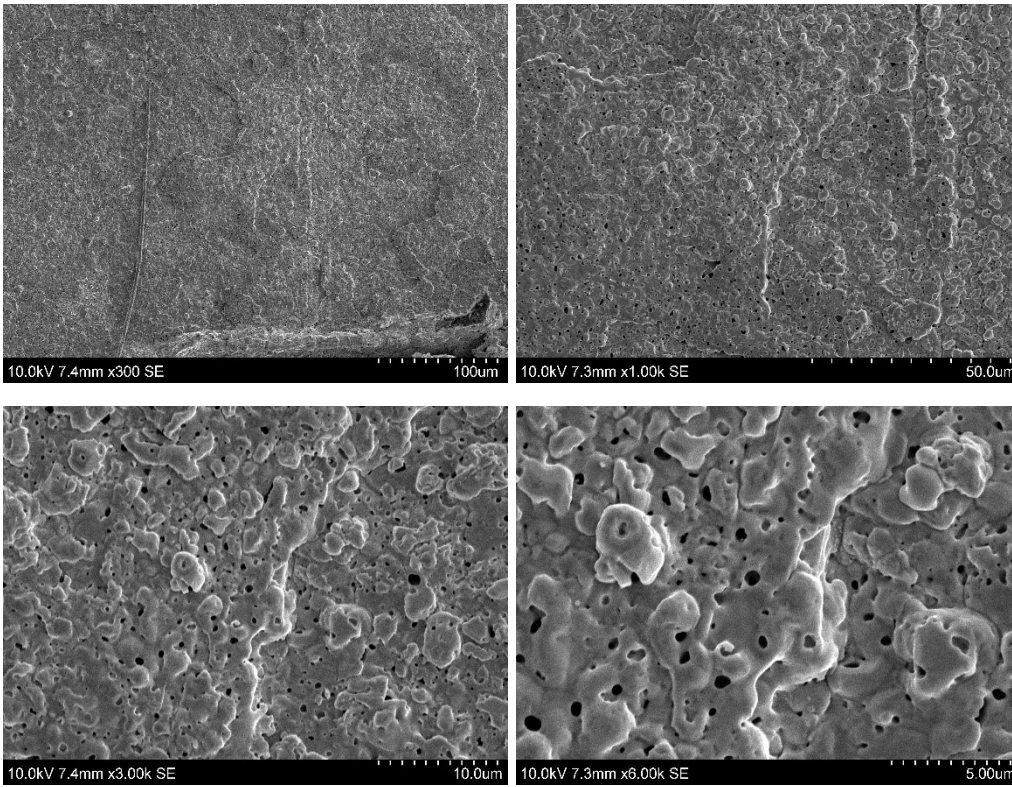
A) Area 1



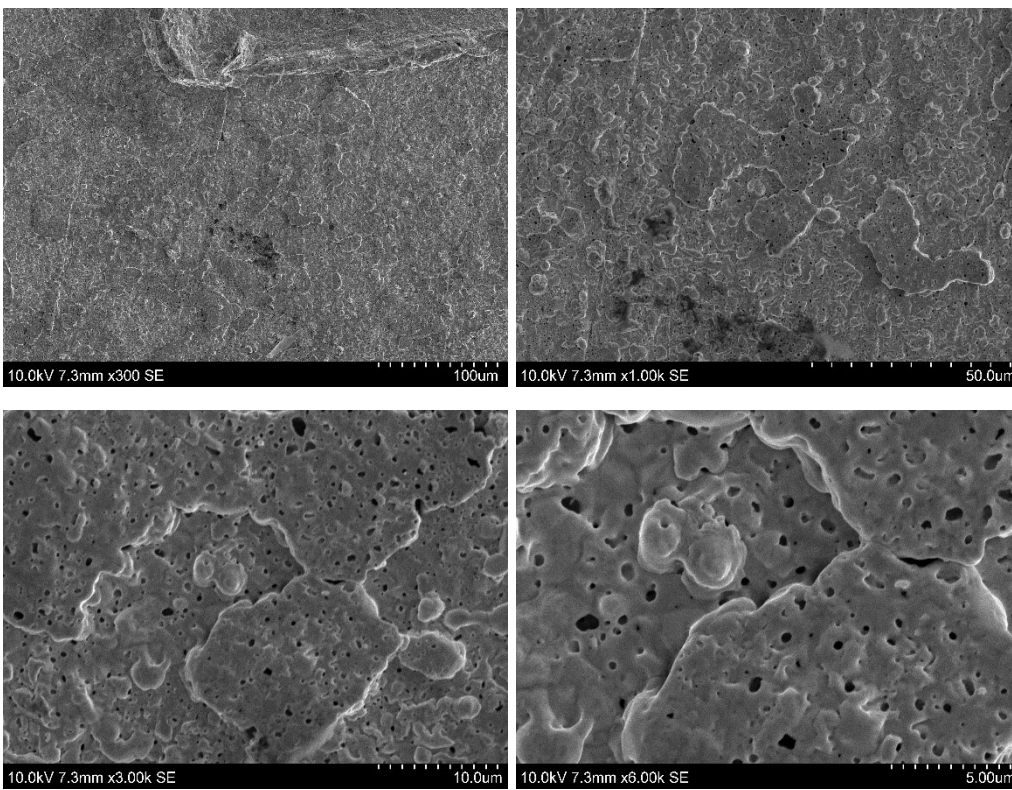
B) Area 2



C) Area 3

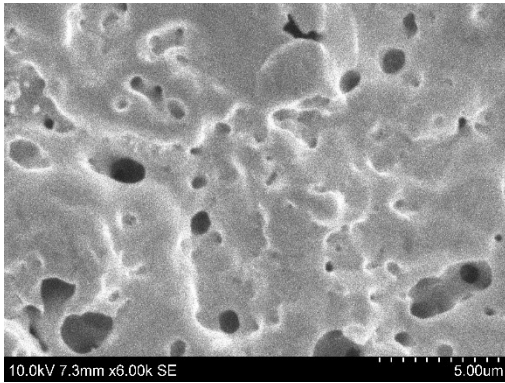
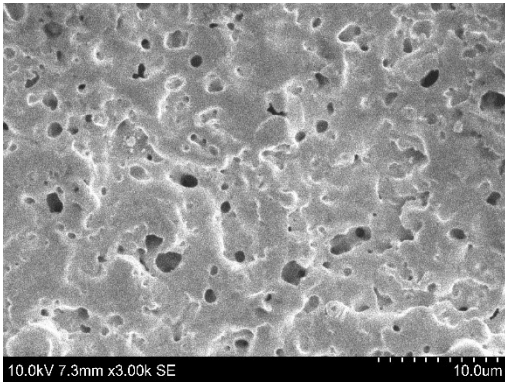
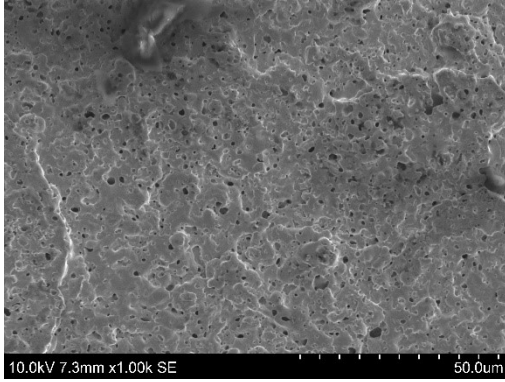
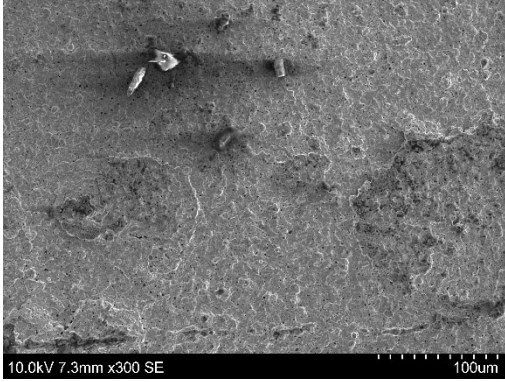


D) Area 4

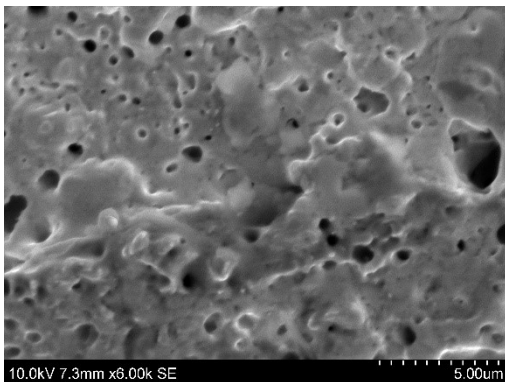
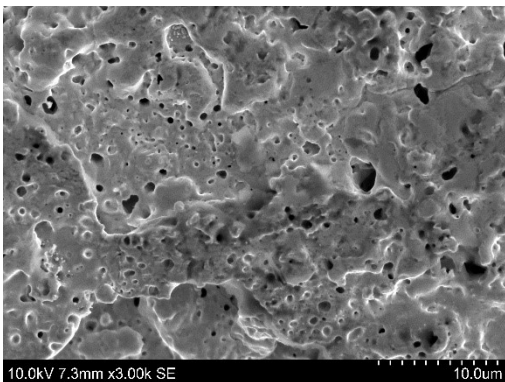
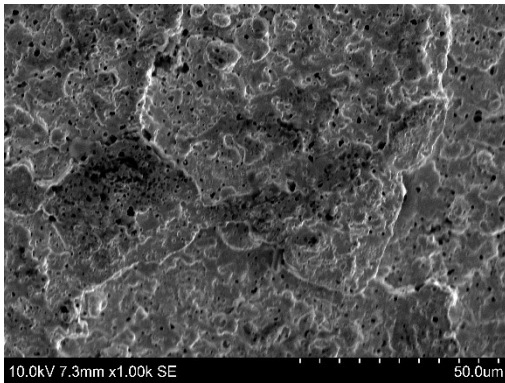
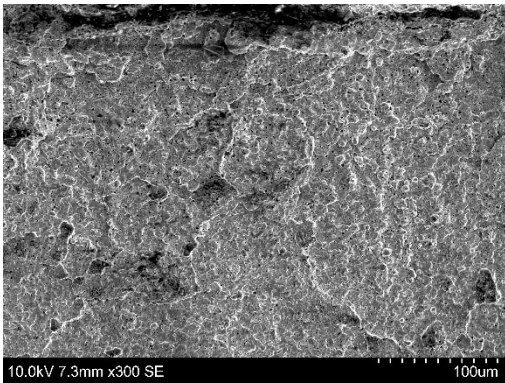


3. 36h experiment catalyst images

A) Area 1

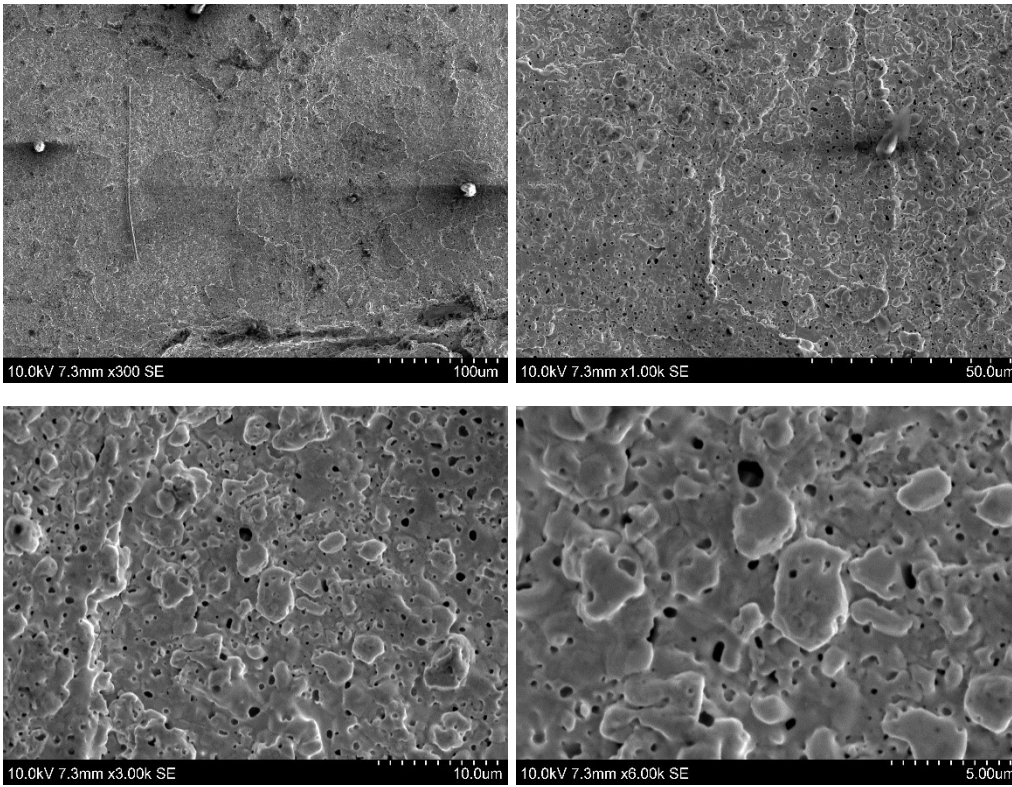


B) Area 2

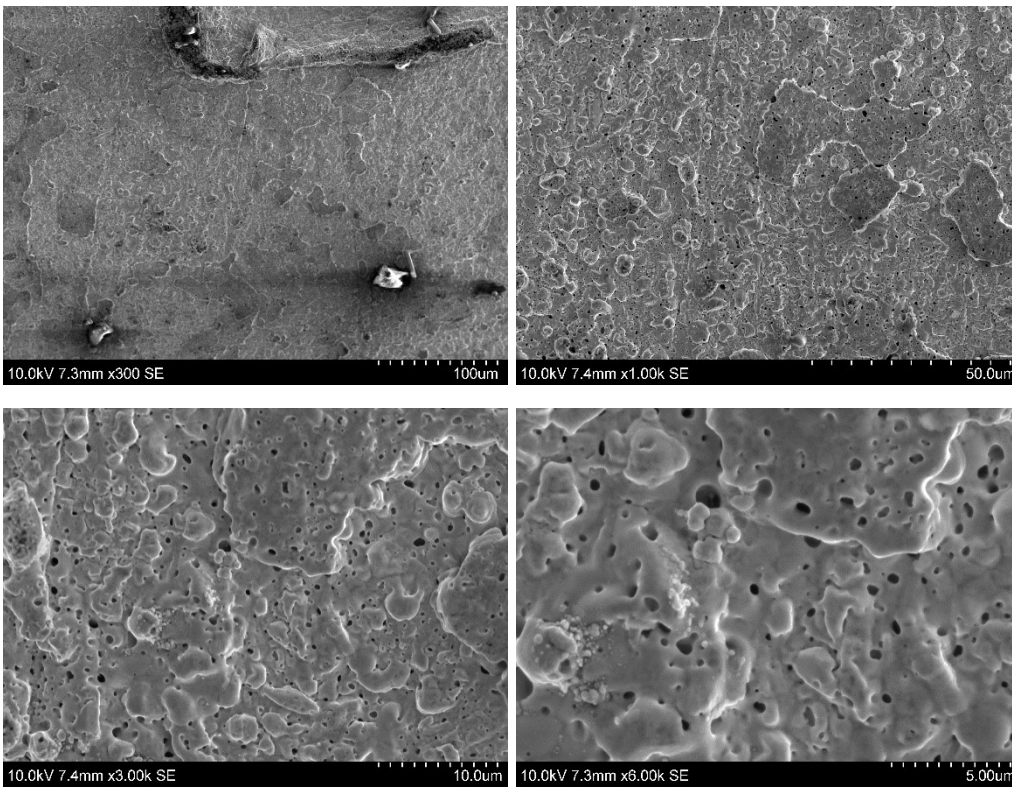




C) Area 3

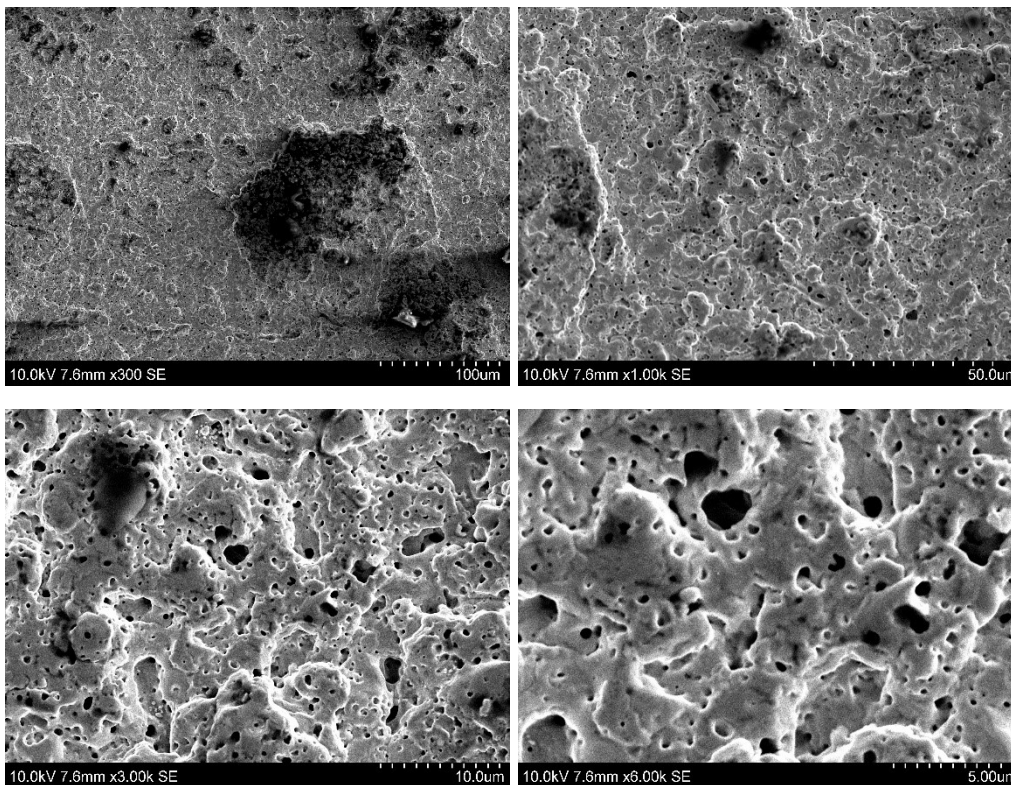


D) Area 4

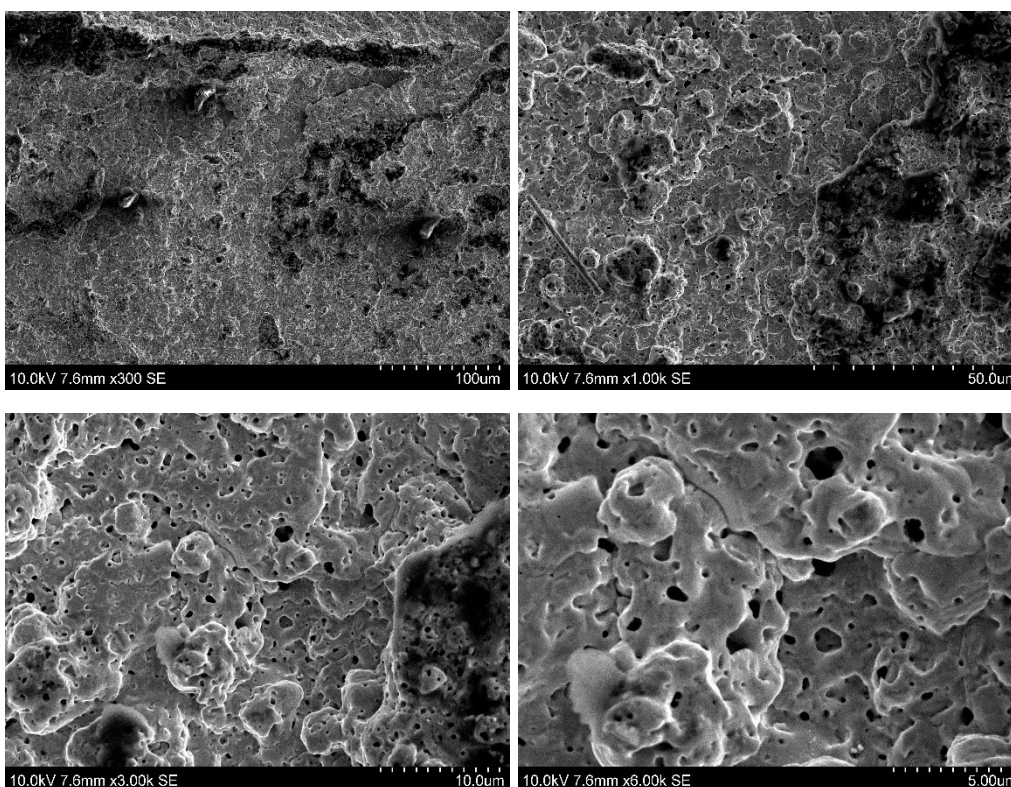


4. 84h experiment catalyst images

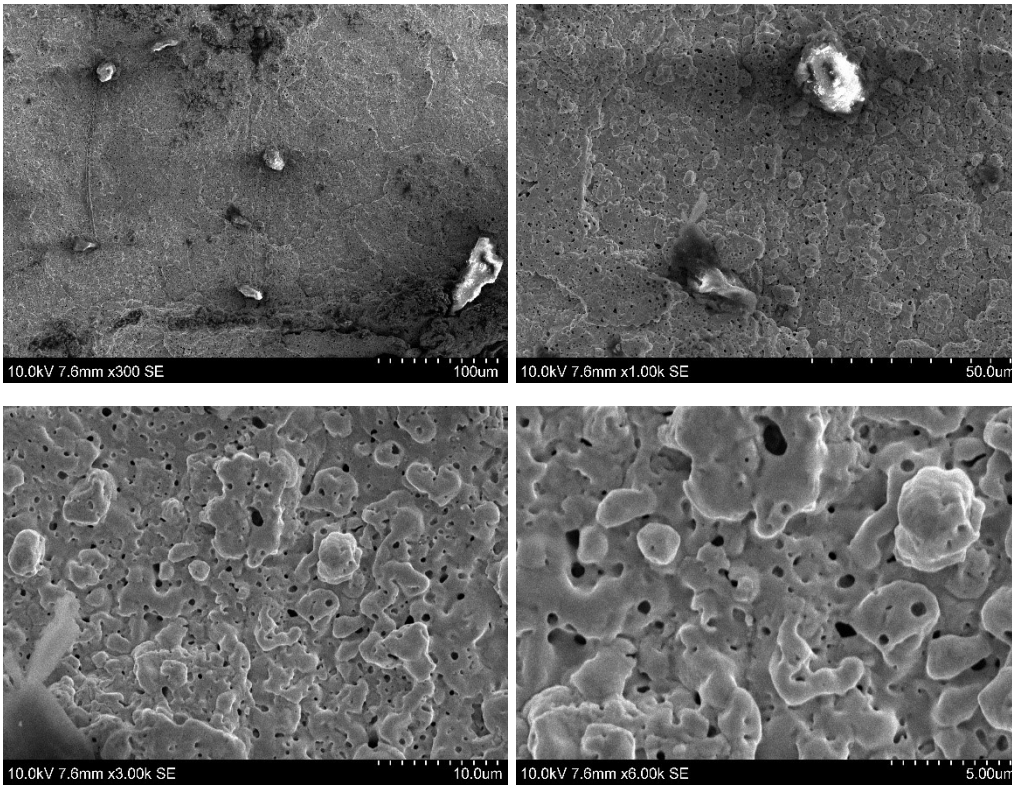
A) Area 1



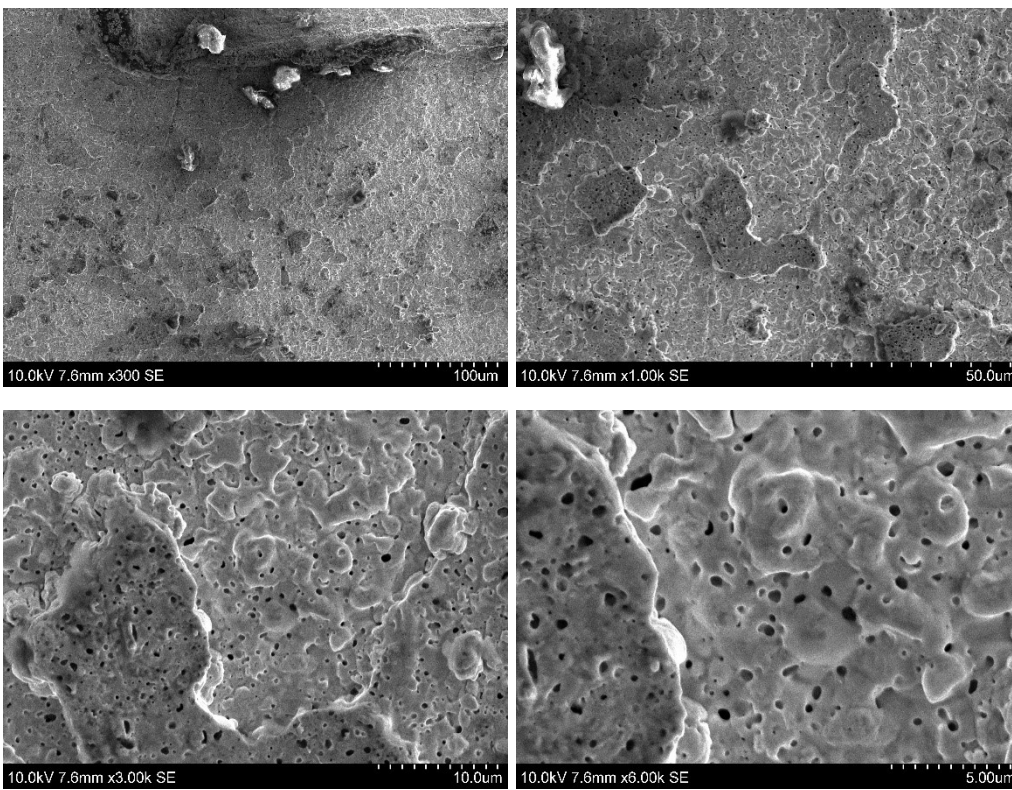
B) Area 2



C) Area 3



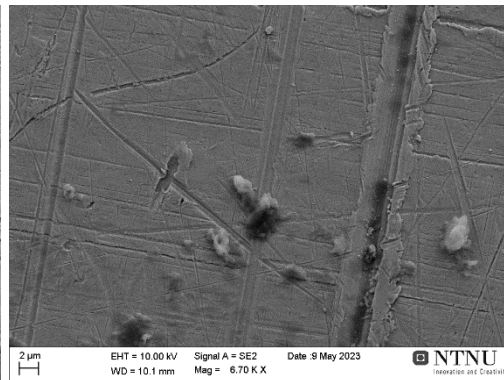
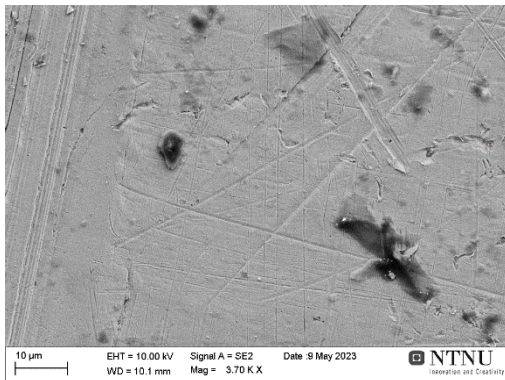
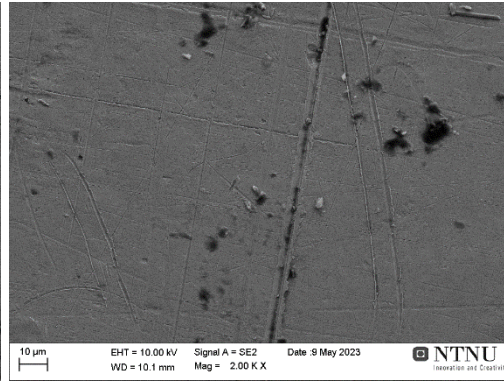
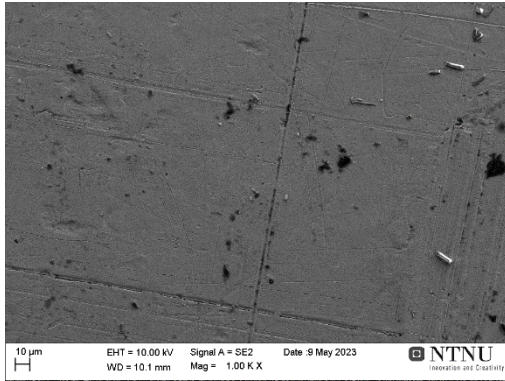
D) Area 4



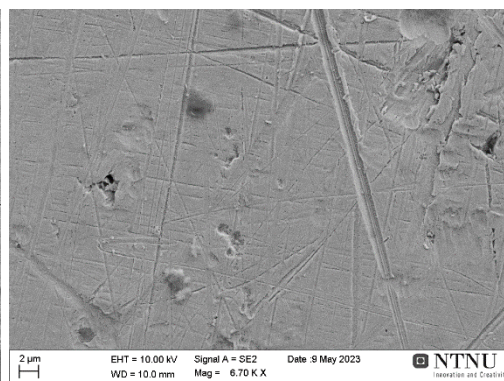
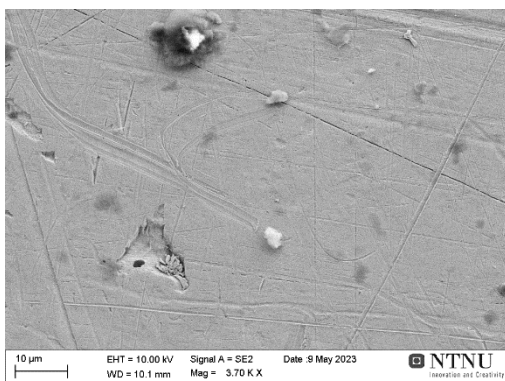
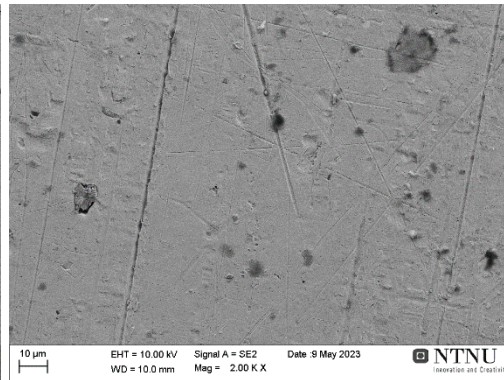
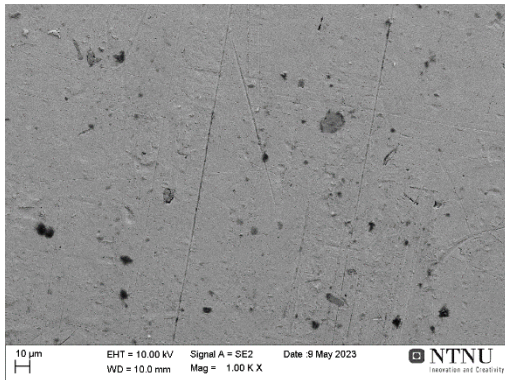


# Appendix E – Syngas Oxidation with water vapour experiment

1. Fresh images of the catalyst
  - A) Area 1

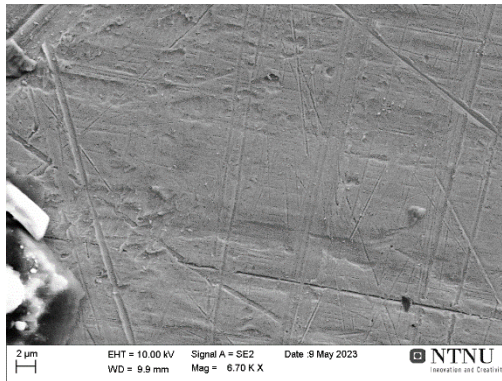
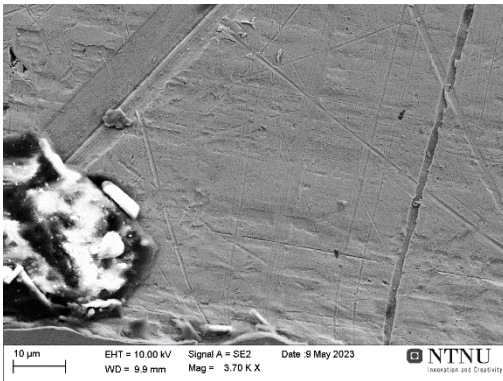
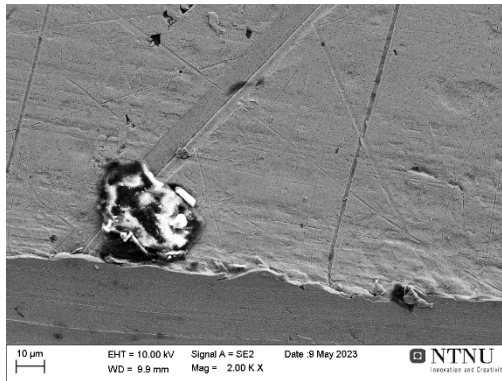
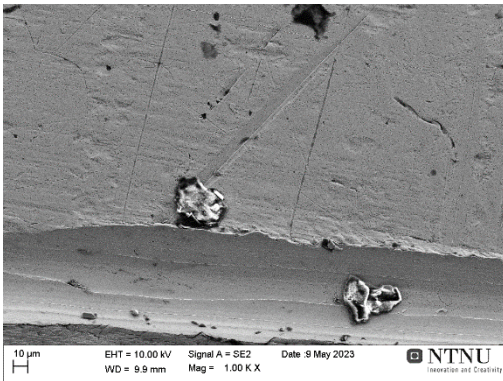


## B) Area 2

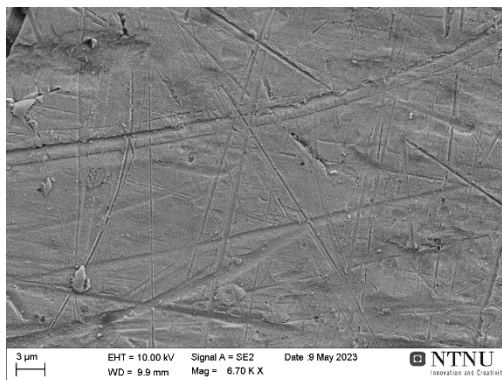
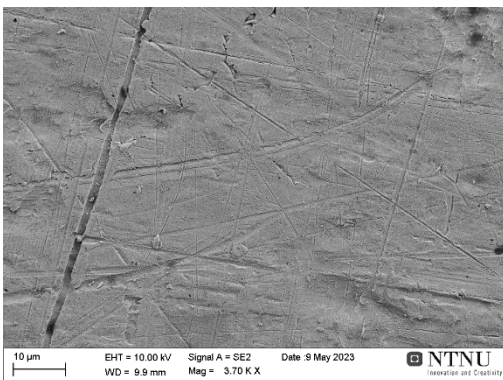
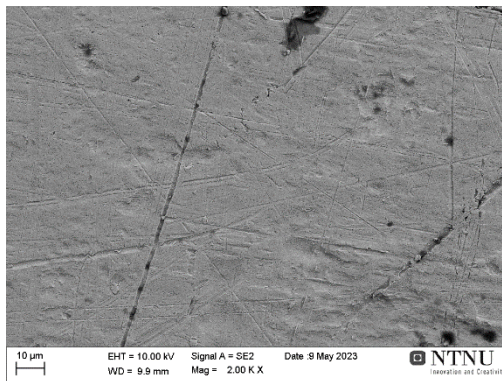
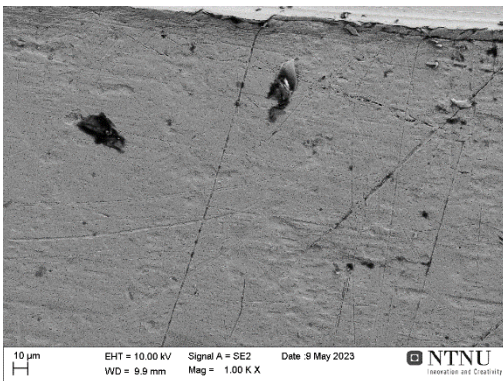




### C) Area 3



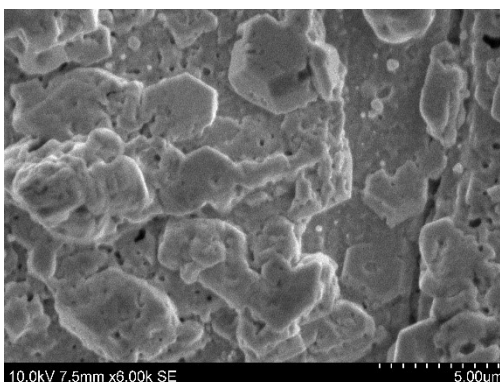
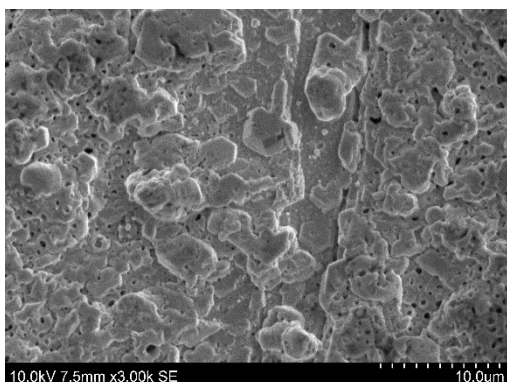
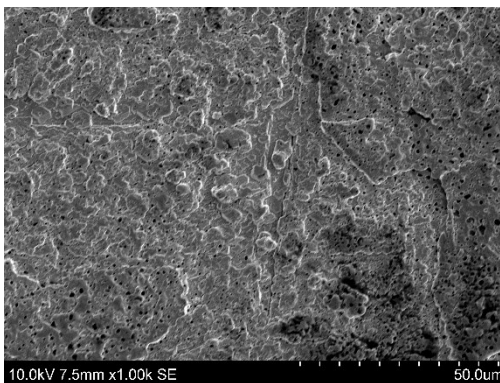
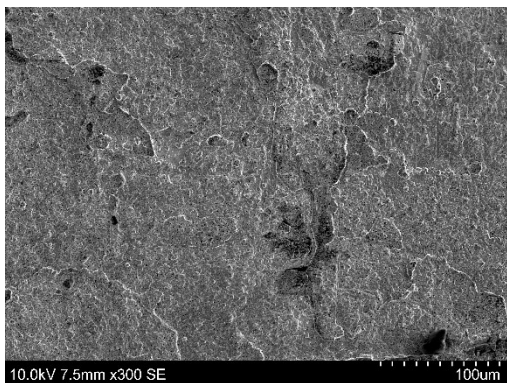
### D) Area 4



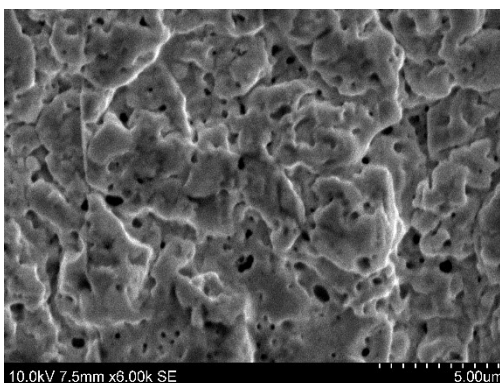
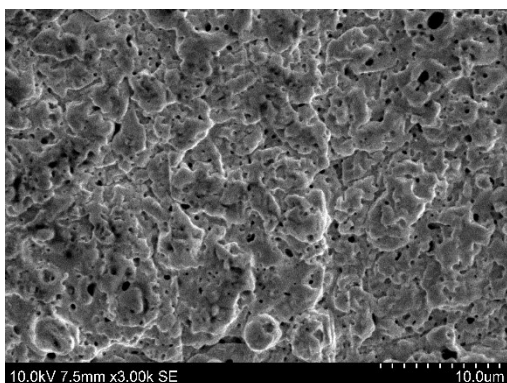
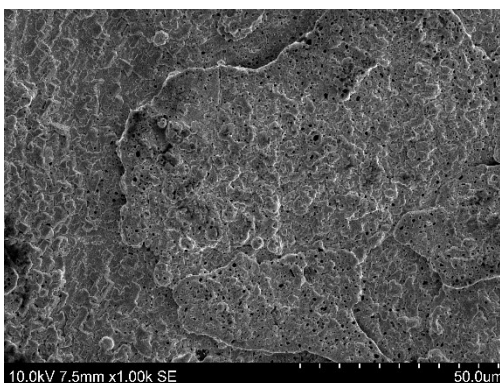
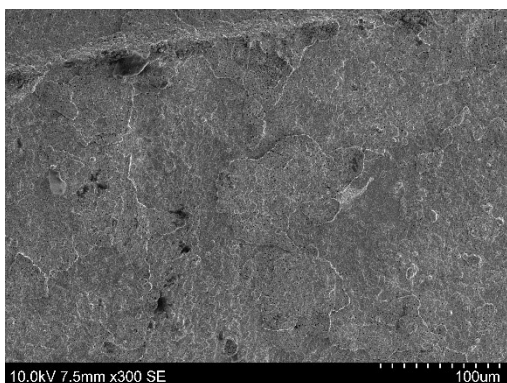


2. 12h experiment catalyst images

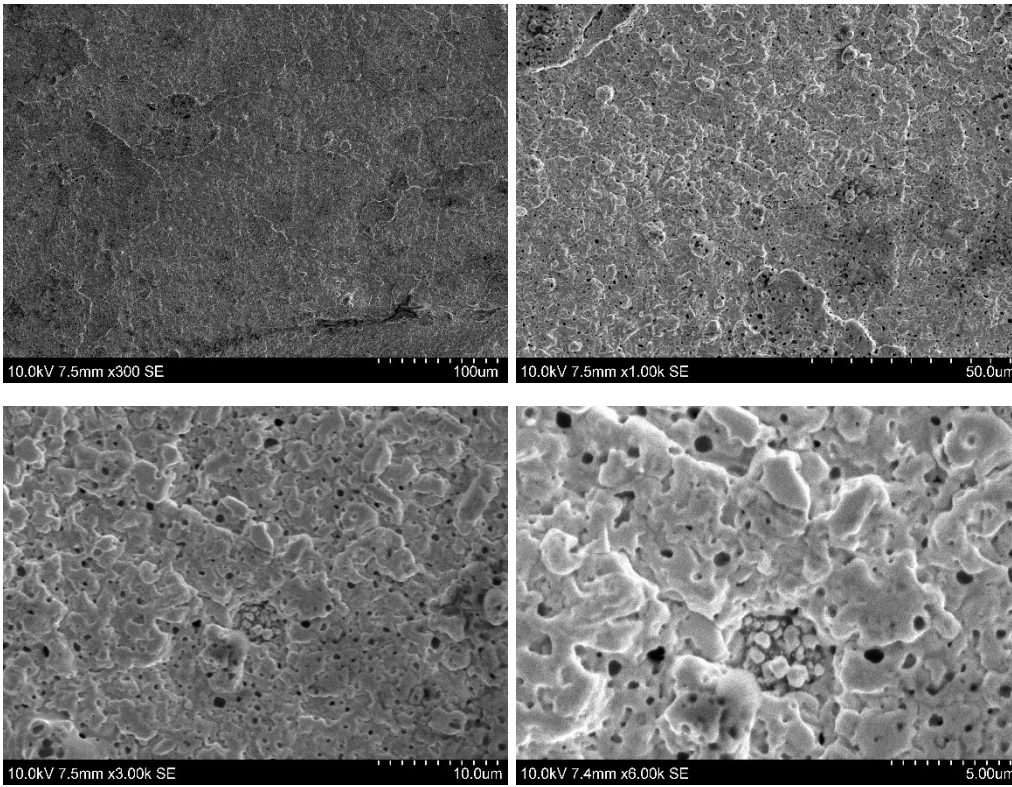
A) Area 1



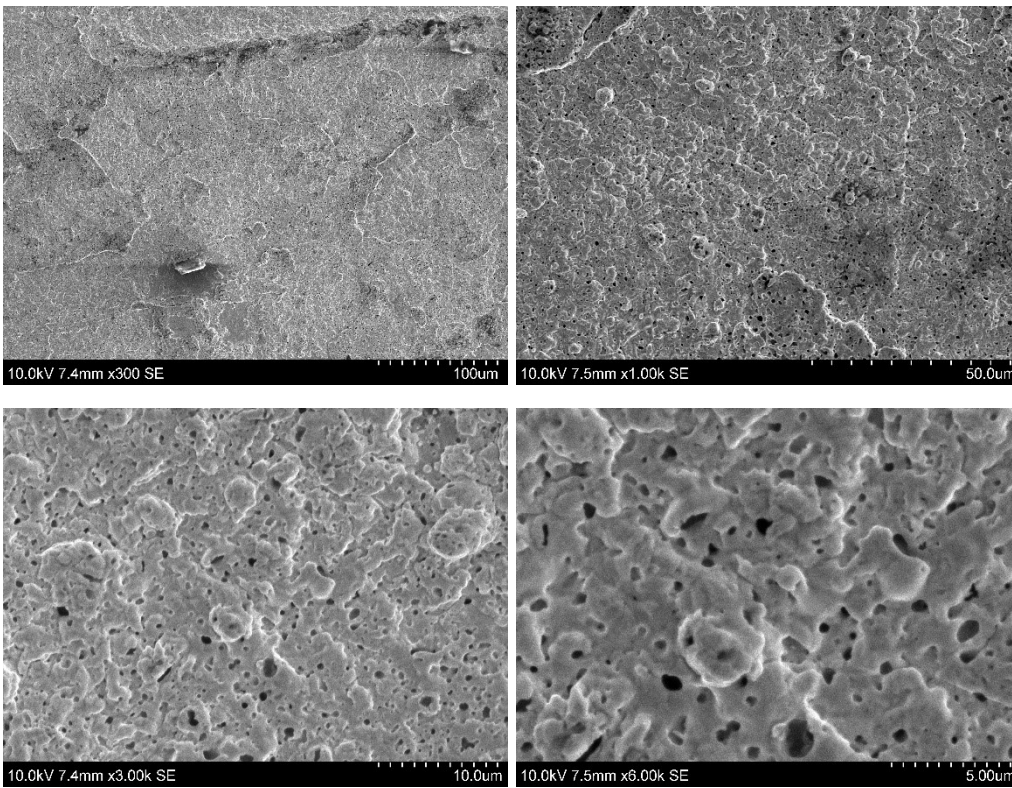
B) Area 2



C) Area 3

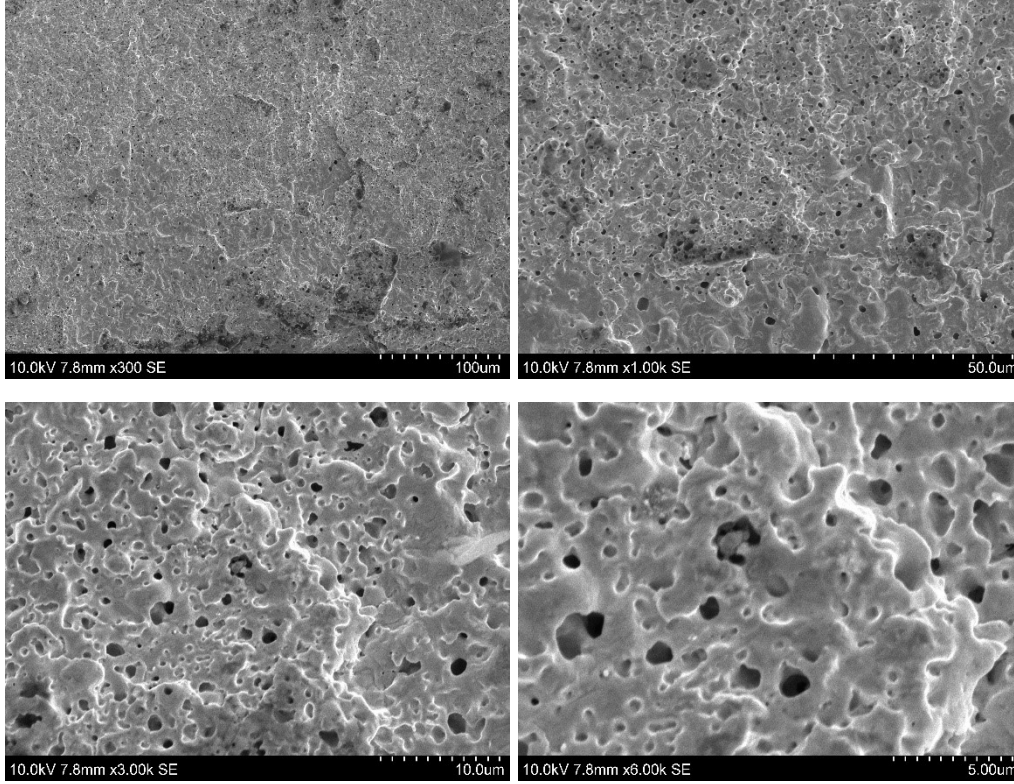


D) Area 4

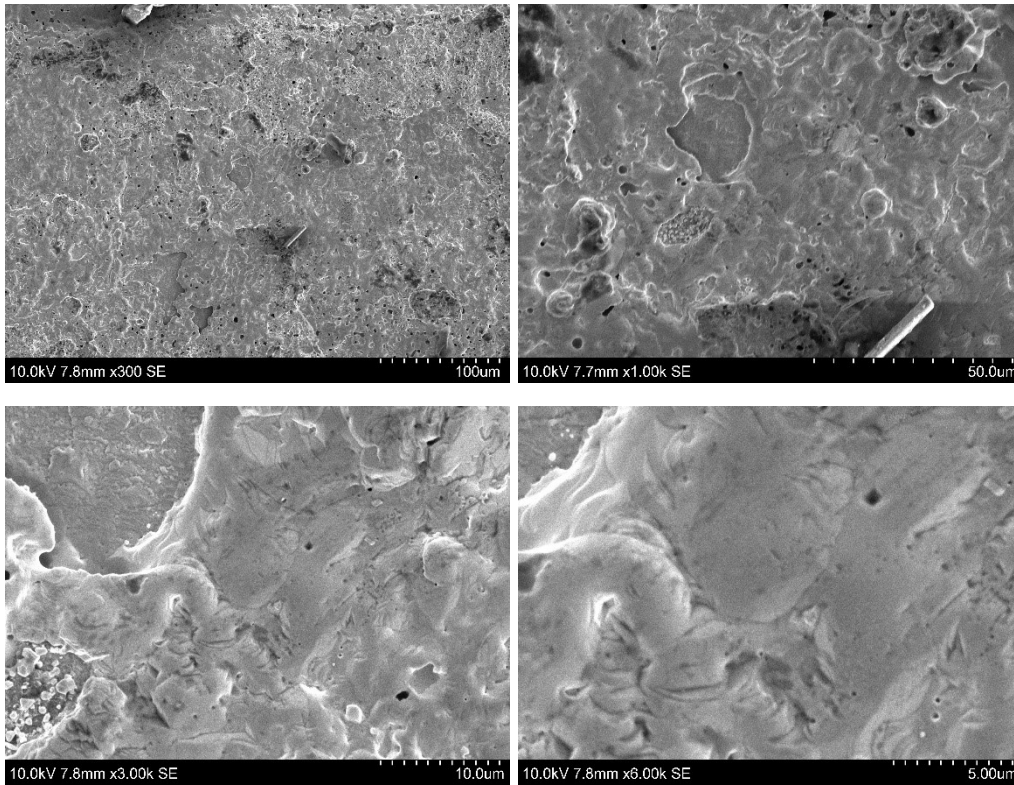


3. 36h experiment catalyst images

A) Area 1

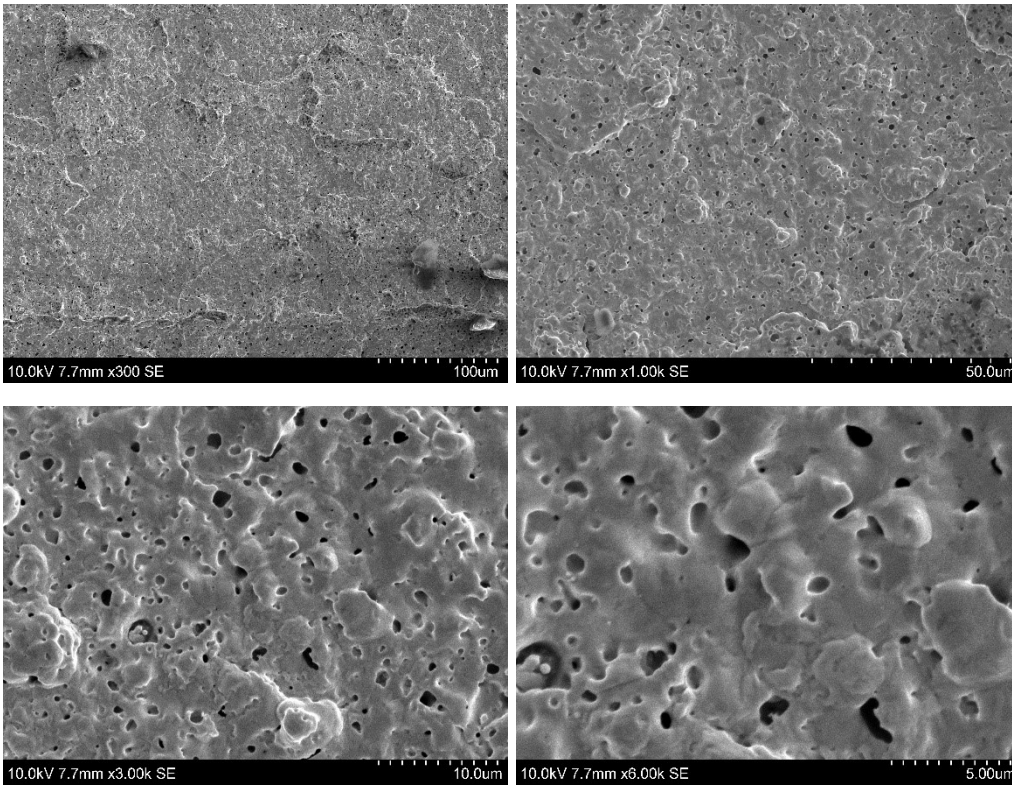


B) Area 2

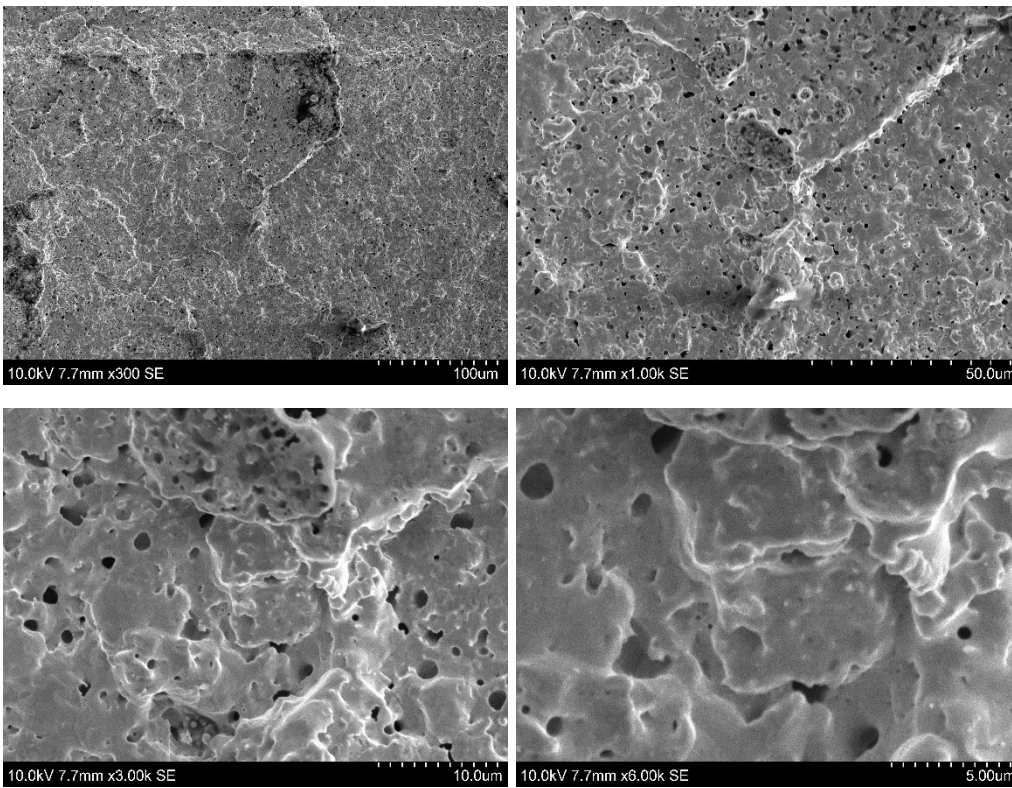




C) Area 3

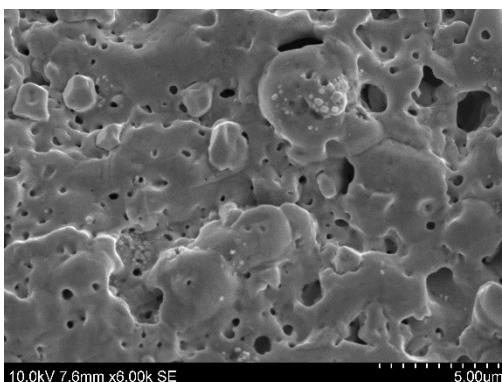
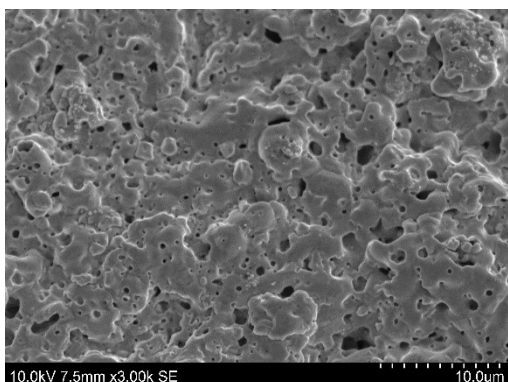
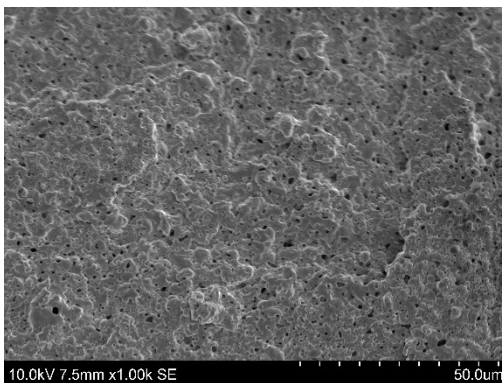
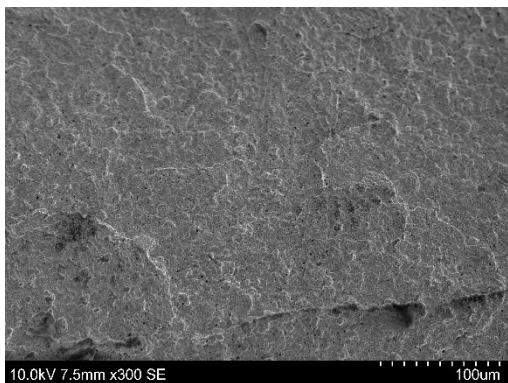


D) Area 4

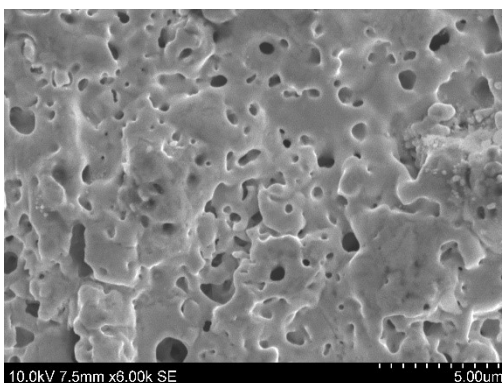
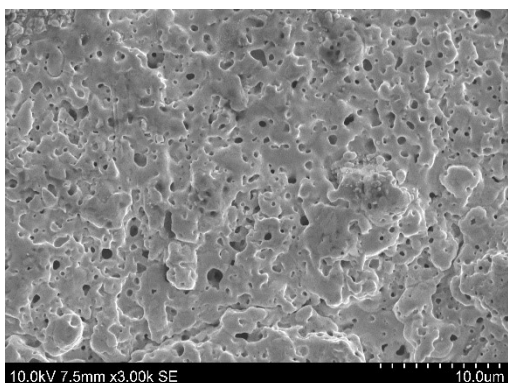
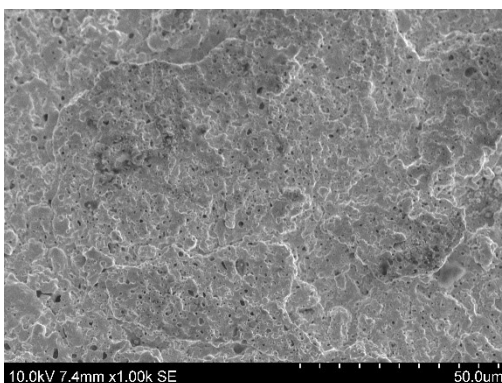
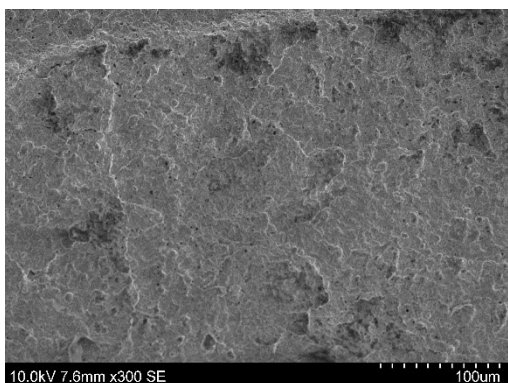


4. 84h experiment catalyst images

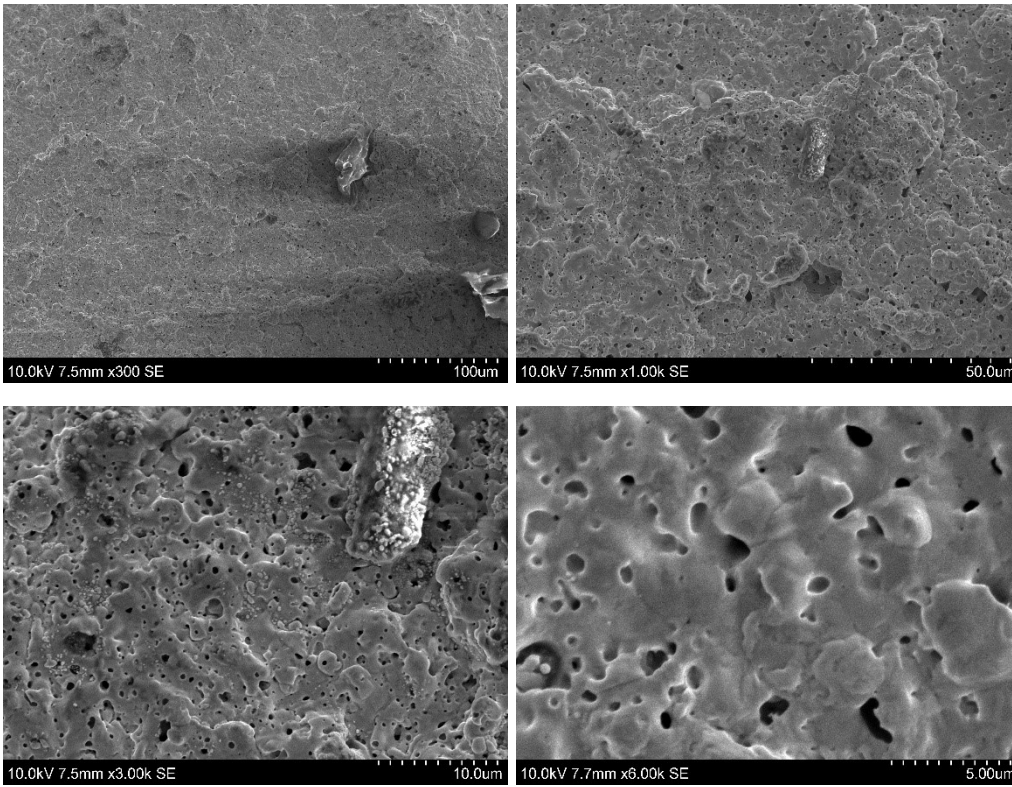
A) Area 1



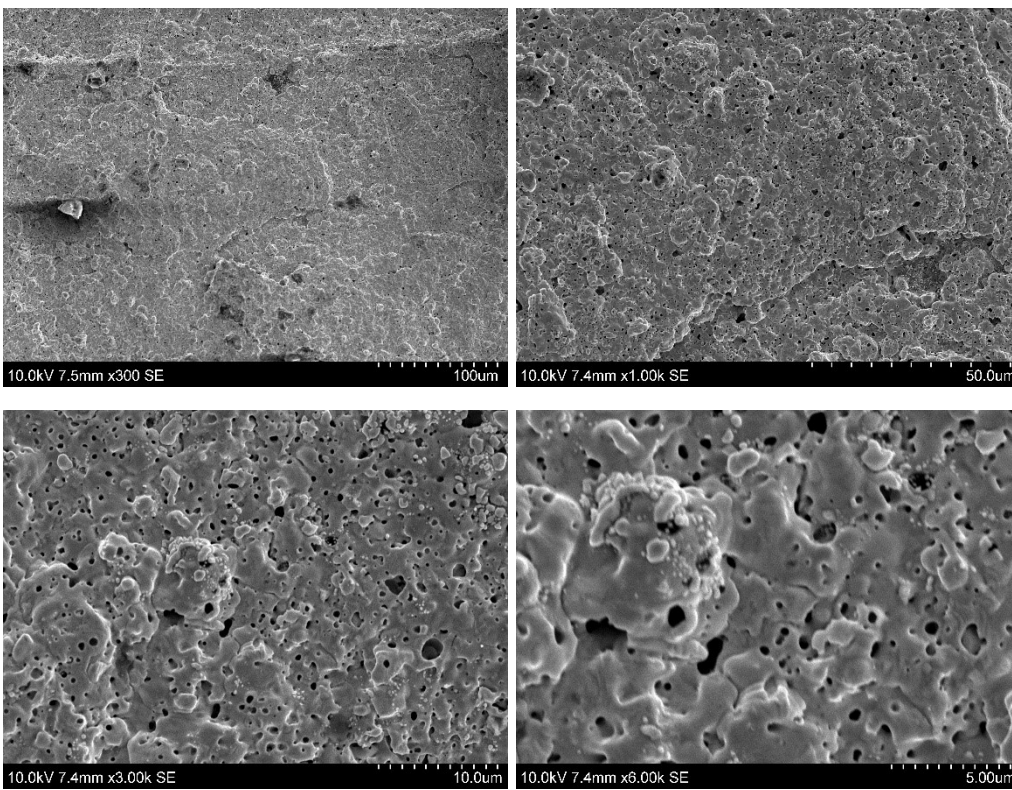
B) Area 2



C) Area 3



D) Area 4



## **Appendix F – Risk Assessment**

The risk assessment is offered together with safety precautions and dangers related to this study is presented in aforementioned chapter. It must be noted that the risk assessment also contains the safety precautions and dangers of the specialization project during the autumn of 2022 [28]. The risk assessment can be reviewed in the portal of risk assessment with ID number 51097.



## Appendix G – Elemental analysis of silver

1) K.A Rasmussen analysis



# ANALYSERAPPORT

Analyse:	Resultat:	Analysemetode:
Al	<5 ppm	ICP-spektroskopi
Au	<5 ppm	-----"
Bi	<5 ppm	-----"
Cd	<10 ppm	-----"
Cr	<10 ppm	-----"
Cu	23 ppm	-----"
Fe	0,6 ppm	-----"
Ni	<3 ppm	-----"
Pb	<5 ppm	-----"
Pd	2,8 ppm	-----"
Pt	<5 ppm	-----"
Se	<5 ppm	-----"
Te	<5 ppm	-----"
Zn	0,8 ppm	-----"
Sn	<10 ppm	-----"
Mn	<10 ppm	-----"
Si	0,9 ppm	-----"
Ca	4 ppm	-----"

2) Goodfellow official



## 99.95% Silver Rod 10mm dia

Ag

Product Code: AG00-RD-000140

Purity: 99.95%

Diameter: 10mm

Temper: As Drawn

Length: 10mm - 1000mm

## Typical Analysis

Na: 1 PPM

Pb: 1 PPM

Zn: 5 PPM

Cu: 70 PPM

Fe: 5 PPM



 **NTNU**

Norwegian University of  
Science and Technology