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DEVELOPMENT OF CATALYTIC SUBSTRATES FOR METHANE DECOMPOSITION REACTORS

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Resumo

O hidrogénio tem sido considerado como um pilar fundamental para uma descarbonização energética mais rápida. No entanto, a produção atual de hidrogénio é baseada em processos não sustentáveis, altamente poluentes e que consomem muita energia, como a reformação de hidrocarbonetos. Assim, a decomposição do metano surge como uma alternativa promissora para uma transição rápida para a produção de hidrogénio sem emissões de CO_x . Esta reação é geralmente realizada a altas temperaturas ($> 1200^\circ\text{C}$) e com sistemas complexos. O uso de catalisadores permite reduzir as temperaturas usadas (500°C a 650°C), o que requer menos energia e permite o uso das atuais infraestruturas de gás natural. No entanto, a decomposição catalítica de metano tem como desvantagens a rápida desativação do catalisador e acumulação de carbono; a utilização de um contactor e um processo de regeneração cíclica permitiram melhorar a vida útil do catalisador. Os catalisadores à base de níquel estão a ser amplamente estudados devido à sua alta atividade a baixas temperaturas. Além disso, os filmes catalíticos devem ser finos e com alta área superficial em relação ao volume para favorecerem a reação. O método de deposição é também crucial para permitir produzir um filme estável, uniforme e altamente ativo. Neste estudo, filmes finos de $\text{Ni}/\text{Al}_2\text{O}_3\text{-SiO}_2$ foram depositados em substratos de vidro através de duas técnicas diferentes, impressão a tela e spray, e testados num reator do tipo contactor desenvolvido internamente para a decomposição catalítica de metano.

Para a preparação de substratos por impressão a tela, a distância de encaixe da tela ao substrato foi selecionada como parâmetro de estudo. O tamanho de partícula do catalisador, a adesão ao substrato, a carga do catalisador e a microestrutura do filme são exemplos dos principais fatores analisados e que afetam o desempenho catalítico dos filmes. Além disso, também foi realizado um estudo reológico sobre a pasta. Assim, demonstrou-se uma correlação entre a distância e o aumento tanto na carga catalítica como na espessura do filme nos substratos; as cargas obtidas tinham uma gama entre $1,5\text{-}2,5\text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$. Todos os filmes apresentaram fissuras e não tinham uniformidade, podendo estar relacionado com o processo de secagem. Observou-se ainda uma falta de adesão nos filmes com maior carga, o que causou o descolamento do filme do substrato durante a reação. Em geral, os filmes com cargas menores apresentaram maior atividade e maior estabilidade. Já no caso dos filmes depositados por spray, para altos valores de carga ($> 7,0\text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$), foi observada uma maior resistência à difusão e uma elevada instabilidade estrutural. Para a mesma carga ($2,5\text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$), os substratos preparados por spray apresentaram maior atividade catalítica e estabilidade.

Os resultados do estudo comparativo forneceram informações valiosas sobre as técnicas de deposição de filmes finos e o seu efeito na decomposição catalítica de metano em baixa temperatura. No entanto, há necessidade de estudar os desafios relacionados à adesão do filme e à não uniformidade observada nos substratos catalíticos produzidos por impressão por tela. O trabalho futuro deve concentrar-se em melhorar a adesão do filme, o uso de técnicas

alternativas de secagem e a exploração de diferentes substratos e catalisadores adequados para otimizar o processo.

Palavras Chave: Decomposição de metano; catalisador de níquel; impressão por tela; spray.

Abstract

Hydrogen has been pointed as a key pillar for a faster energy decarbonization. However, current hydrogen production is based on non-sustainable, highly polluting and energy-intensive processes, such as hydrocarbon reforming. As such, methane decomposition emerges as a promising alternative to enable a swift transition by producing CO_x-free hydrogen. Methane decomposition reaction is usually performed at high temperatures (above 1200 °C) and complex systems. The use of catalysts allows the production of hydrogen at lower temperatures (500-650°C), which requires less energy and enables the use of current infrastructures for natural gas. However, catalytic methane decomposition suffers from rapid catalyst deactivation and carbon clogging. The use of a contactor reactor design and a cyclic regeneration process was reported to improve the catalyst lifetime. Nickel-based catalysts have been widely investigated due to their high activity at this temperature range. Thin catalytic films have unique properties that can favor the reaction, such as high surface area to volume ratio. Therefore, determining the most effective deposition method to produce a stable, well-defined and highly active film is crucial. In this study, Ni/Al₂O₃-SiO₂ thin films were deposited by two different techniques on glass substrates, screen printing and wet spray, and tested in an in-house developed contactor reactor for catalytic methane decomposition.

For the screen printing coated substrates, the snap-off distance was selected as study parameter. The catalyst particle size, adhesion to the substrate, catalyst loading and film microstructure are examples of key factors analyzed that impact the catalytic performance of the films. Besides that, a rheological study about the screen printing paste was also conducted. A correlation between the snap-off distance and an increase in both catalytic loading and film thickness was demonstrated for the screen printed substrates. The obtained loadings were in the range of 1.5-2.5 mg_{cat}·cm⁻². All screen printed films exhibited cracks and a non-uniform film, which are possibly related to the unsuitable drying process. Moreover, a lack of adhesion was observed for the films with higher loading, which caused detachment during the reaction. In general, the films with lower loadings presented an increased activity and higher stability. In the case of the films deposited by wet spray, for high loading levels (>7.0 mg_{cat}·cm⁻²) an increased diffusion resistance and high structural instability was observed. For the same loading (2.5 mg_{cat}·cm⁻²), wet spray exhibited a higher catalytic activity and structural stability.

The findings from this comparative study provided valuable insight into the techniques for deposition of thin films and its effect on the performance of low-temperature catalytic methane decomposition. However, challenges regarding film adhesion and non-uniformity observed in screen printing coated substrates need to be addressed. Future research focus on enhancing the film adhesion, adopting alternative drying techniques, and exploring different substrates and suitable catalysts to further optimize the process must be performed.

Keywords: Methane decomposition; Nickel catalyst; Screen printing; Wet spray.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

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Index

1	Introduction.....	1
2	Context and State of the art.....	5
2.1	Catalytic Methane Decomposition	5
2.1.1	Reaction mechanism and carbon deposition	6
2.1.2	Reaction conditions and their effects on the equilibrium.....	8
2.1.3	Reaction Catalysts	9
2.1.4	Reactor Design	13
2.1.5	Deactivation and regeneration.....	15
2.2	Screen Printing.....	16
2.2.1	Components of the paste	17
2.2.2	Screen printer parameters.....	20
2.2.3	Other parameters	21
3	Materials and Methods	22
3.1	Experimental procedure.....	22
3.1.1	Catalytic paste formulation and deposition through screen printing.....	22
3.1.2	Wet Spray deposition.....	23
3.1.3	Reactional CMD setup	24
3.2	Physicochemical analysis methods	25
3.2.1	Rheological tests.....	25
3.2.2	Laser diffraction	25
3.2.3	Scanning electron microscopy and energy-dispersive X-ray spectroscopy	26
3.2.4	Reaction performance.....	26
4	Results and Discussion	27
4.1	Rheological properties	27
4.2	Characterization of printed layers	30
4.3	Catalytic Tests.....	34
4.4	<i>Post-mortem</i> characterization	35
4.5	Regeneration Test	36

4.6	Comparison with wet spray	38
5	Conclusion.....	43
6	Assessment of the work done	45
6.1	Objectives achieved.....	45
6.2	Future work.....	45
7	References	46
	Annex A - Supplementary figures	53
	Appendix A - Methane decomposition adsorption mechanism	57
	Appendix B - Examples of Ni catalysts	58
	Appendix C - Solvents Properties.....	59
C.1	Propane-1,2-diol	59
C.2	α -Terpineol.....	59
C.3	Propane-2-ol	60
C.4	Water	60
	Appendix D - Granulometric data.....	61
D.1	Number	61
D.2	Volume	61
D.3	Surface Area	62
	Appendix E - Three Interval Thixotropy Test	63
	Appendix F - SEM images and EDS analysis of the screen printed substrates	64
F.1	Top view and EDS	64
F.1.1	SP-1.0.....	64
F.1.2	SP-1.2.....	65
F.1.3	SP-1.5.....	66
F.1.4	SP-1.8.....	67
F.2	Cross-section.....	68
F.2.1	SP-1.0.....	68
F.2.2	SP-1.2.....	69

F.2.3 SP-1.5.....	70
F.2.4 SP-1.8.....	71
Appendix G - <i>Post-mortem</i> SEM images and EDS analysis of the screen printed substrates..	72
G.1 SP-1.0	72
G.2 SP-1.2	73
G.3 SP-1.5	73
G.4 SP-1.8	74
Appendix H - Regeneration test.....	75
Appendix I - SEM images and EDS analysis of substrates coated by wet spray	76
I.1 Top-view and EDS analysis	76
I.1.1 Spray-2.5	76
I.1.2 SP-7.5	77
I.2 Cross section.....	77
I.2.1 Spray 2.5.....	77
I.2.2 Spray-7.5	78

List of figures

Figure 1 - Global greenhouse gas emissions under different scenarios (extracted from Ref. [4]).	1
Figure 2 - Hydrogen usage (A); hydrogen demand over the years (B); hydrogen cost according to the production source (C); hydrogen production methods (D) (extracted from Ref. [13]).	2
Figure 3 - Representation of different carbon growth mechanisms: tip-growth (A) and base growth (B) (extracted from Ref. [33]).	8
Figure 4 - Equilibrium conversion of methane by varying temperature and pressure in Aspen Plus v10 (extracted from Ref. [42]).	9
Figure 5 - Methane decomposition behavior with temperature range, and carbon products and catalysts. Catalysts: 1–Ni-based, 2–Fe-based, 3–carbon-based, 4–summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5–non-catalytic decomposition. Carbon products: CF–carbon filaments, TC–turbostratic carbon, GC–graphitic carbon, AmC–amorphous carbon (extracted from Ref. [49]).	10
Figure 6 - Schematic representation of the screen printing process (extracted from Ref. [23]).	17
Figure 7 - Schematic representation of some screen printing parameters (extracted from Ref. [85]).	20
Figure 8 - Screen printing setup (A); Screen printed substrates and their respective identification at the top (B).	23
Figure 9 - Wet spray setup (A); Sprayed substrates (B).	24
Figure 10 - Viscosity-shear rate curves for propane-1,2-diol pastes varying the time spent on the ball milling: 1 h (A); 2 h (B); 3 h (C).	27
Figure 11 - Variation of the substrate loading with the snap-off distance for the prepared SP films.	31
Figure 12 - Top-view SEM images (BSE mode, 15 kV) of the SP-0.8 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure 12.C (D).	32
Figure 13 - Cross-sectional SEM images of the SP-0.8 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).	33
Figure 14 - H ₂ activity over time for the substrates coated by screen printing: 10 h (A); zoom of first 2 h (B).	34
Figure 15 - Substrates coated by screen printing after the reaction and their respective identification at the top.	35
Figure 16 - Top-view SEM images of post-mortem samples: SP-1.0 - x300 (A) and x3000 (B); and SP-1.2 - x300 (C) and x3000 (D).	36
Figure 17 - Comparison of the H ₂ activity over time between cyclic regeneration with hydrogen and unregenerated systems using SP-1.0 sample. For the regenerated catalyst, only the decomposition steps of each cycle are displayed.	37

Figure 18 - SEM images of the wet spray samples: cross section - x1000 (A) and top-view - x300 (B) for Spray-2.5; cross section - x1000 (C) and top-view - x300 (D) for Spray-7.5.	40
Figure 19 - H_2 activity over time for the catalytic substrates coated by wet spray method.	40
Figure 20 - Naked eye post-mortem images of: Spray-2.5 (A); Spray-7.5 (B); Spray-9.2 (C).	41
Figure 21 - Post-mortem SEM images of Spray-2.5 sample: top view of the center of - x300 (A); top view approximation of the center of Spray-2.5 - x6700 (B).	42
Figure 22 - H_2 activity over time comparison between: Spray-2.5, SP-1.0 and SP-1.8.	42

List of tables

<i>Table 1 - Viscosity (Pa·s) values obtained at 0.01 s⁻¹ for the studied pastes.</i>	<i>28</i>
<i>Table 2 - Recovery at the end of the 3ITT method and necessary time to achieve 80 % of the initial viscosity.</i>	<i>29</i>
<i>Table 3 - Thixotropic Index of the selected pastes.</i>	<i>29</i>
<i>Table 4 - Information about the screen printing coatings.</i>	<i>30</i>
<i>Table 5 - Thickness variation of the prepared screen printed substrates.</i>	<i>33</i>
<i>Table 6 - Reaction performance parameters obtained for the samples coated by screen printing.</i>	<i>35</i>
<i>Table 7 - Information about the wet spray coatings.</i>	<i>38</i>
<i>Table 8 - Reaction performance parameters of the samples coated by wet spray.</i>	<i>41</i>

Notation and Glossary

List of Acronyms

BSE	Backscattered electron
CCS	Carbon capture and sequestration
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
CMD	Catalytic methane decomposition
DFT	Density function theory
EDS	Energy-dispersive X-ray spectroscopy
<i>fcc</i>	Face-centered-cube
FBR	Fixed bed reactor
FLBR	Fluidized bed reactor
GC	Gas chromatography
GHG	Greenhouse gases
MSI	Metal-support interaction
MMR	Molten metal reactor
NDCs	National determined contributions
NPT	Normal pressure and temperature conditions
PBR	Plasma bed reactor
PSA	Pressure swing adsorption
SP	Screen printing
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
SS	Stainless steal
SMR	Steam methane reforming
TRL	Technology readiness level
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
3ITT	3 interval thixotropy test

Nomenclature

a_{H_2}	Hydrogen production activity	$g_{H_2} \cdot g_{cat}^{-1} \cdot h^{-1}$
Y_c	Carbon yield	$g_c \cdot g_{cat}^{-1}$
F_{CH_4}	Inlet methane volumetric flowrate	$mL \cdot min^{-1}$
F_{H_2}	Produced hydrogen volumetric flowrate	$mL \cdot min^{-1}$
M_{H_2}	Molar mass of hydrogen	$g \cdot mol^{-1}$
$\dot{m}_{H_2}$	Produced hydrogen mass flowrate	$g_{H_2} \cdot h^{-1}$
ρ_{H_2}	Hydrogen density	$g_{H_2} \cdot mL^{-1}$
W	Catalyst mass	g_{cat}
T_{H_2}	Total volumetric production of hydrogen	mL
V_m	Molar volume	$mL \cdot mol^{-1}$
X_{H_2}	Hydrogen conversion	
X_{CH_4}	Methane conversion	
y_i	Molar (volumetric) fraction of component <i>i</i> on the stream	

1 Introduction

Industrialization, the engine for economic expansion and urbanization, and the growth of the global population, has accelerated the growing demand on energy. The overexploitation of fossil fuels resources, and deforestation, have contributed to the ever-increasing concentration of greenhouse gases (GHG) in the atmosphere. This has resulted in carbon dioxide levels reaching an unprecedented historical high of 420 ppm [1]. In response to the worsening global climate change, the Paris Agreement, signed in 2015, aims to hold the increase in average global temperature to well below 2 °C above pre-industrial levels, achieving carbon neutrality by 2050 [2]. In 2020, each country submitted its own strategic plan. The Nationally Determined Contributions (NDCs) took into account the Energy Trilemma [3]: affordability (energy equity), reliability (energy security) and mitigation of environmental impacts (environmental sustainability). Figure 1 shows the different scenarios predicted by United Nations Environment Programme (UNEP) about pollutants emissions in the next decades [4]. In consequence of this scenario, the carbon dioxide (CO₂) credit price has been increasing, reaching almost 110 €·ton_{CO₂}⁻¹ and expecting to hit 200 €·ton_{CO₂}⁻¹ in 2030 [5].

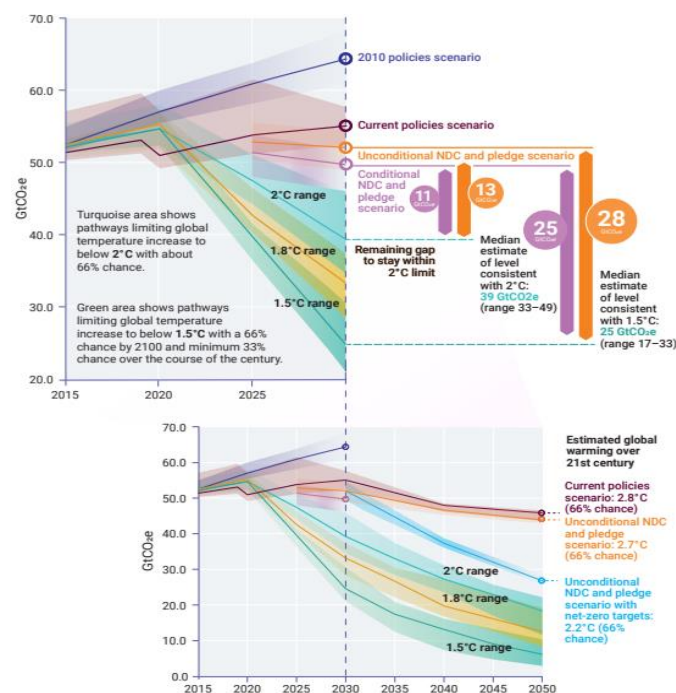


Figure 1 - Global greenhouse gas emissions under different scenarios (extracted from Ref. [4]).

The world needs to quickly adopt renewable energy sources, making the development of new technologies based on solar, wind, and wave energy imperative. However, despite being abundant, these alternative sources are intermittent in nature, which requires efficient energy storage solutions. Hydrogen (H₂) emerged as a promising chemical energy vector, which can be used for storing excess of renewable electricity through processes such as water electrolysis or as an alternative fuel to replace fossil fuels. In spite of H₂ being the most abundant element in the universe, there is no natural resource of H₂ and, consequently, it needs to be extracted

from other abundant sources in a cost-effective way. Accordingly to Ashik *et al.* [6], the annual H_2 production would have to be multiplied *ca.* 100 times to fulfill the World's demand for fossil fuels. This marks the basis of the so-called H_2 economy, where hydrogen would be used directly in fuel cells and H_2 turbines, or indirectly in reverse petrochemistry and production of high-energy-density synthetic fuels like methanol. In terms of energy density, H_2 has one of the highest quantities of energy per mass ($120.2 \text{ MJ}\cdot\text{kg}^{-1}$), almost triple than other popular fuels, as natural gas ($48.7 \text{ MJ}\cdot\text{kg}^{-1}$) and others liquid hydrocarbons [7]. However, its volumetric energy density represents a problem concerning storage and transportation.

Depending on the production method, H_2 is typically classified by a code of colors. *Grey* H_2 is produced by reforming processes, mainly Steam Methane Reforming (SMR), representing almost 80 % of the global hydrogen production. SMR is a mature, well-developed, and cost-effective technology for hydrogen production. It enables the production of the cheapest hydrogen, priced at *ca.* $1.4 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ and $2.7 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ before and after the Russia-Ukraine War, respectively [8, 9]. This affordability is primarily due to the price of natural gas. However, SMR inevitably emits between 8 and 12 kg of CO_2 for each kg of hydrogen produced [10]. Another drawback of this technology is the necessity of subsequent steps, as the water gas shift reaction and a further separation of the produced hydrogen from the by-products. *Blue* H_2 is the combination of the *grey* H_2 method and the carbon capture and sequestration (CCS) technology. It is an important transition approach, but lately this technology has shown some controversial and environmental problems - energy is necessary to power the CCS equipment and leakage phenomena are not yet fully understood [11]. *Blue* H_2 price is also strictly dependent on the natural gas price, being on range of $2 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ and $4 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ [8, 12]. On the other hand, *green* H_2 is produced by water electrolysis utilizing electricity provided by renewable sources. Despite being a zero-emission technique, the actual poor efficiency and high cost of the electrolyzers are current disadvantages. *Green* H_2 average price changes drastically with the natural resource, *i.e.* it can be *ca.* $6 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ when solar energy is utilized, and *ca.* $4 \text{ €}\cdot\text{kg}_{H_2}^{-1}$ for wind energy [9]. Figure 2 summarizes data on H_2 production, demand and final use [13].

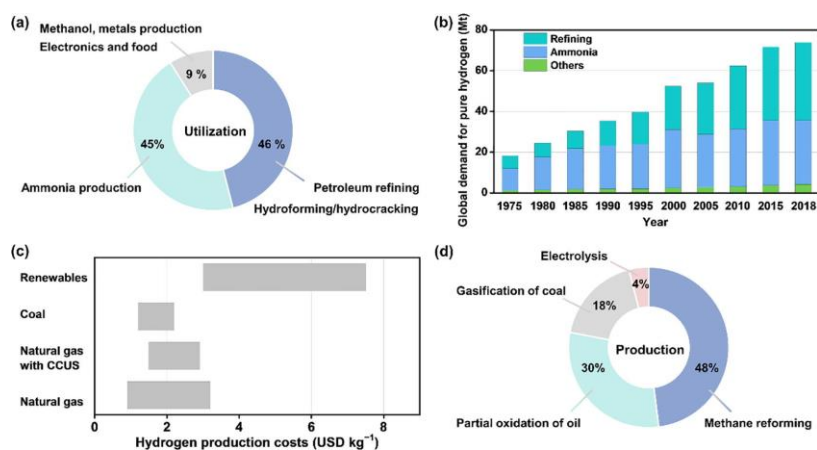
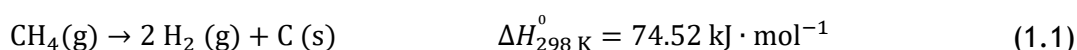


Figure 2 - Hydrogen usage (A); hydrogen demand over the years (B); hydrogen cost according to the production source (C); hydrogen production methods (D) (extracted from Ref. [13]).

Besides water electrolysis, alternative processes to produce clean H₂ must be developed. Methane decomposition, also known as methane pyrolysis, is a particularly relevant alternative to the current state-of-the-art technologies for H₂ production, allowing a soft transition of energy systems [14]. Methane molecule, the main compound in natural gas, has the highest H/C ratio between all the hydrocarbons, therefore being one of the best sources of hydrogen. H₂ produced from pyrolysis is coded as *turquoise* if methane (CH₄) comes from natural gas source, resulting in clean H₂ with estimated costs comparable to the reforming process. However, this process is even more interesting if biogas or biomethane are used, since it provides a negative carbon balance. Methane decomposition, an endothermic reaction, splits CH₄ into H₂ and solid carbon (C) - equation (1.1).



Methane is a highly stable molecule with a tetrahedral geometrical structure composed by four strong C-H bonds, each one with an energy bond of 434 kJ·mol⁻¹ [6]. Taking this into account, high reaction temperatures, in the order of 1200~1300 °C [15], are necessary to achieve high conversions in uncatalyzed processes. Therefore, catalyst employment is a crucial aspect to reduce the activation energy, providing an operation pathway that performs at lower temperatures - the so-called catalytic methane decomposition (CMD). However, the carbon clogging represents one of the major drawbacks of CMD, given that it is responsible for catalyst deactivation. Typically, the catalyzed rate is faster than the diffusion through the catalyst, making carbon to encapsulate the catalyst or even cause its detachment from the support, reducing the catalytic activity and eventually causing full deactivation. The addition of a regeneration process is a possible alternative to mitigate this effect; UPORTO and Pixel Voltaic teams proved that a cyclic interfacial regeneration with H₂ favors the reverse reaction and consequently regenerate the catalysts [16]. Zhang *et al.* [17] made an economical study that compare the viability of this technology with other methods in different scenarios, including complete catalyst regeneration and the sale of the carbon product versus the reverse. According to this study, although an expected higher price for CO₂ emissions in the future, the technology would not be profitable if the catalyst is not recycled. Besides that, further competitiveness can be achieved by utilizing the carbon product. If the carbon is removed from the reactor without detrimental effects, the economic exploitation of the by-product will be important to make the process more competitive, reducing the hydrogen price, with the expectation to reach the range of 1.6-2.2 €·kg_{H₂}⁻¹ [18].

CMD is currently in the research and development stage, with ongoing efforts focused on optimizing reaction conditions, identifying highly active catalysts capable of long-term activity despite carbon accumulation, and designing reactors that can address mass transfer challenges. Commonly metal-based or carbonaceous catalysts are used, being transition metals (d-elements) embedded in a support the ones responsible for the best results to date [15].

Among these, Ni and Fe are widely used due to their low cost, good catalytic activity, and stability at low temperature operation [19]. The use of metal catalysts also promotes the formation of highly graphitic carbon materials, which have much higher commercial value, due to their unique properties in applications such as electrodes, bipolar plates, Na-ion batteries, rubber, construction or asphalts [20]. The high surface area and porosity presented by inorganic oxides, like Al_2O_3 and SiO_2 , make them interesting as support materials, improving the metal dispersion and resistance against sintering [19].

In the field of catalysis, catalytic thin films have emerged as an important area of research, mainly because of their unique properties compared to traditional bulk catalysts [21]. These films are deposited over a substrate and usually present a thickness in the range of a few nanometers to micrometers, which gives them a large surface area to volume ratio. The substrate also plays a crucial role, since it directly influences the adhesion, stability and durability of the film. Additionally, the substrate can affect important performance factors, such as thermal stability, chemical resistance and mechanical strength of the thin film. Some commonly used thin film deposition techniques include physical vapor deposition, chemical vapor deposition, and atomic layer deposition [22]. Yet, screen printing is an example of a promising alternative, since it is a simple, reproducible, scalable, and versatile technique [23].

In the present work, a paste composed by Ni/ Al_2O_3 - SiO_2 will be deposited by screen printing technique on different substrates and tested on a planar cell reactor. The objective is to evaluate how the paste composition and its rheological properties, as well as the film thickness influence the screen printing parameters, and finally the CMD performance; a comparison with other catalyst deposition technologies was also conducted. The work was performed at LEPABE and Pixel Voltaic, a spin-off company from University of Porto. Currently, both teams are involved in the EU-funded 112CO2 project [24], leading the development of low-temperature catalytic methane decomposition for CO_x-free H₂ production.

2 Context and State of the art

2.1 Catalytic Methane Decomposition

Methane decomposition is a reaction that allows the conversion of methane to hydrogen without direct emissions of GHG. Since the reaction is 100 % selective, solid carbon is the only byproduct. This technology can promote a faster transition solution towards hydrogen economy. Another potential advantage is the possibility to produce hydrogen from biogas, which can reduce the greenhouse-effect by actively removing CO₂ from the atmosphere at very competitive cost [25]. The operation without catalyst needs temperatures over 1200 °C to achieve reasonable conversion levels, being energy intensive and harming the cost-effectiveness of the process. By using catalysts, the activation energy of methane decomposition can be decreased, which allows a drastically reduction of the operation temperature and superior reaction velocity. Currently, Fe and Ni are the most used materials, due to higher activity and low costs [26]. It is a consensus in the literature that initial catalytic activity relies on the physico-chemical characteristics of the catalyst, such as particle size or defects, while long-term activity can be correlated to physical properties, like the interaction of metal and support, dispersion capability, surface area and pore volume [6, 26]. A balance among the methane dissociation rate, carbon diffusion and growth are essential. The catalyst deactivation as result of coking represents a barrier to the improvement of this technology. Therefore, in spite of the many advantages of CMD, it is not yet considered a mature technique because of some obstacles preventing its application on an industrial scale. Hence, a comprehensive study of all parameters is crucial to achieve optimal operational conditions.

Currently, Monolith Inc presents one of the most advanced methane pyrolysis technologies in order to produce simultaneously carbon black and hydrogen from natural gas, through a plasma reactor (2200-2400 °C) [27, 28]. Their technology is at a technology readiness level (TRL) 9 and the Olive Creek Plant is the first industrial/commercial methane pyrolysis facility. BASF thermal pyrolysis (1200-1400 °C), based on a moving carbon bed, is being tested on laboratory (TRL 4), expecting to evolve to a pilot scale shortly [28]. In the reactor developed by BASF, carbon black grains are fed into the reactor top and, due to gravity, they move to the methane fed on the bottom. The generated carbon joins these grains since the reaction takes place on its surface, allowing continuous withdraw [29]. In contrast Hazer Group, utilizes a thermocatalytic process (750-900 °C) by continuously adding Fe catalyst on a three-stage fluidized bed reactor, being one of the most developed CMD technologies, *i.e.*, TRL 5 [26, 28]. C-Zero is also developing a thermocatalytic process currently at TRL 4, producing hydrogen on a packed bed reactor with molten-Ni-based catalyst [28]. These processes represent promising

alternatives that are experiencing rapid growth and scaling efforts, despite challenges related to system complexity and energy-intensive operations. Pixel Voltaic's process is the only one being operated at lower temperatures (500-650 °C) for more than 4000 h using Ni-based catalysts [25]; however, it is only expected to reach TRL 4 within 1 year.

Despite significant research efforts devoted to methane decomposition, several knowledge gaps in this field remain. Most of the research focus on catalytic studies and high temperature processes, such as plasma and molten metal reactors, as well as sustainable ways to feed this heat, for example through concentrated solar power [30, 31]. Few works are found about low temperature processes (500-650 °C), either regarding operating conditions, reactor design and performance evaluation. Therefore, considering its potential for achieving high conversion levels through a simpler and less energy-intensive process, low temperature methane decomposition should be explored as a promising and viable alternative to existing established processes.

2.1.1 Reaction mechanism and carbon deposition

Understanding the reaction mechanism is essential for the development and optimization of the catalytic process since it will enable the design of more efficient catalysts and reaction conditions. The most accepted theory indicates that the reaction of cracking only involves a sequential dehydrogenation of the methane molecule on an active site of the catalyst surface and finally hydrogen desorption [32-34]. Briefly, CDM reaction mechanism can be resumed in five main steps: (1) chemisorption of methane on the active site of the catalyst; (2) progressive breaking of the four C-H bonds; (3) formation of hydrogen molecule from the adsorbed atomic hydrogen and its emission on gaseous stage; (4) aggregation of the atomic carbon, which can leads to catalyst deactivation, or its diffusion through the bulk catalyst driven by a concentration or temperature gradient; (5) carbon nucleation followed by the formation and growth of carbon products; the carbon production is directly related to the catalyst, namely to its geometry, interface, phase and physicochemical steps [32]. In step (1), the dissociative adsorption and non-dissociative adsorption mechanisms are the prevailing theories, with the dissociative adsorption being the more currently accepted one [33, 35]. On the dissociative mechanism, the chemisorption of methane and the first break of the C-H bond happen simultaneously, while on the non-dissociative one they happen in separate steps. Appendix A (Table A.1) presents the mechanism for both models. Salam *et al.* [36] studied CMD on a Ni/Al₂O₃ (001) catalyst surface and reported that the energy needed to break the first C-H band is much lower than the other three, suggesting that adsorption and the first dehydrogenation can be treated simultaneously (Figure A.1). Regardless of the theory, the kinetic law and the rate-limiting step are not yet completely understood, however, it is widely accepted that adsorption of methane is the most probable limiting step.

In the case of methane decomposition, reaction simulation models, such as density function theory (DFT), can be used to investigate the interactions between the catalyst and the methane molecule at an atomic scale, identify the key reaction intermediates and transition states, and predict the activity of different catalysts. The crystalline structure of the catalyst has a crucial effect on the catalytic activity and stability. Besides the atomic arrangement, defects as vacancies or surface steps can create sites with better adsorption and activation of the methane molecules. For example, in the case of Ni catalysts, the (100) and (110) crystal planes of the face-centered-cube (*fcc*) structure exhibit higher activity for methane decomposition compared to other planes [37]. This phenomenon can be attributed to differences in the surface structure and atomic arrangement, which directly affect the adsorption and reaction mechanism [38]. It is widely accepted that the methane molecules are adsorbed on stepped surfaces and on the active surface Ni (100). According to Wang *et al.* [39] and Gili *et al.*, [40] after the dissociative adsorption, the released carbon will undergo diffusion into the Ni crystal and filaments would rapidly grow on the Ni (111) face of the crystal, which may lead in the Ni crystal to stay on the tip of the growing structure.

Carbon growth poses a significant challenge in the field of CMD, affecting both catalyst/process efficiency and durability. Once the methane molecule is adsorbed and gradually decomposed on the catalyst active site, the resulting carbon species dissolve into the bulk and diffuse through the catalyst particle driven by concentration and temperature gradient. The chemical potential difference between the support, metal and gas interfaces favors the carbon diffusion [32-35]. Simultaneously, the catalyst surface exposed to the gas is hotter than the one facing the support, where the carbon precipitates and forms filaments [33, 35]. If the carbon diffusion rate is higher than deactivation rate, the catalyst can maintain its activity; otherwise, deactivation by carbon accumulation will occur. Hence, the carbon growth is directly related to the catalyst deactivation. According to Ashik *et al.* [32], the carbon formation can affect the CMD activity by the following ways: (1) adsorbing strongly on the active site, blocking the access; (2) encapsulating the metal particle and gradual loss of the catalyst particle; (3) preventing entry into the pores by settling at the entrances; and (4) even blocking the reactor

The growth mechanism is directly affected by the catalyst itself (size of the metal particle, metal loading, support interaction, *etc.*) and the reaction conditions (temperature, gas partial pressure, reactor design, fluid flow, *etc.*) [15, 35]. In accordance with these factors, the carbon produced can grow on the catalyst surface (base-growth) or at the interface between the catalyst and the support (tip-growth). Figure 3 illustrates both mechanisms that can take place simultaneously during the reaction. A strong metal-support interaction (MSI) may promote base growth due to the enhanced binding strength and decreased mobility, while a weak interaction

may favor tip-growth mechanism leading to detachment and lifting of the metal particle [34, 35]. Tip-growth is harmful to the catalyst lifetime, since the catalyst gets separated from the support (or from the bulk for unsupported catalysts), which causes a permanent activity loss [15]. Through these mechanisms, different forms of carbon nanoparticles can be generated during CMD reaction, such as carbon nanofilaments (CNFs) and carbon nanotubes (CNTs). Besides that, under unique conditions, other special structures can also be generated, namely nano-onions, bamboo-shaped and octopus-shaped (Figure A.2 and A.3) [33, 35]. Filamentous carbon is one of the most desirable types of carbon to be produced, since it has a high market value due to interesting mechanical and electrical properties. High value carbon can reduce the final price of hydrogen and make the process more profitable [34].

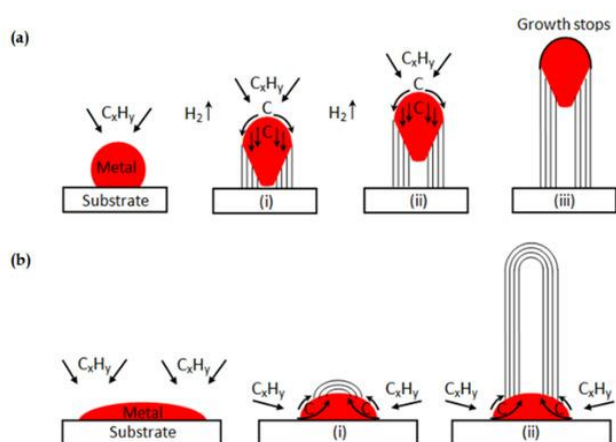


Figure 3 - Representation of different carbon growth mechanisms: tip-growth (A) and base growth (B) (extracted from Ref. [33]).

2.1.2 Reaction conditions and their effects on the equilibrium

The operating pressure and temperature are critical factors that influence the CMD reaction rate and conversion levels. Higher temperatures increase the kinetic energy of the molecules, causing them to move faster and collide more frequently, which consequently increases the reaction rate. This phenomenon is stated by Arrhenius Equation [41]. Non-catalytic methane decomposition needs temperatures above 1000 °C. In the case of CMD, high temperature can be prejudicial to the catalyst, leading to undesirable phenomena, as sintering and a disequilibrium between methane dissociation and carbon diffusion. Pressure enhancement increases the number of collisions between the reactant molecules and the catalyst [41]; however, high pressures may raise the safety concerns and equipment expenses. Moreover, as an equilibrium-limited endothermic reaction, the equilibrium conversion is higher when operating in high temperatures, which can be explained by Le Chatelier's principle [34]. Pérez *et al.* [42] made a simulation study on *Aspen Plus v10* to analyze the effect of pressure and temperature on the equilibrium conversion of uncatalyzed methane decomposition (Figure 4). By their results, it can be observed that high temperature and low pressure favor the equilibrium conversion.

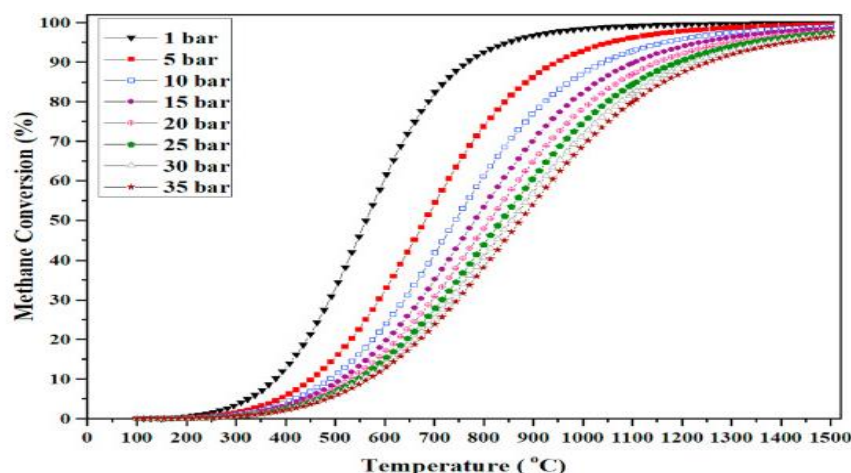


Figure 4 - Equilibrium conversion of methane by varying temperature and pressure in Aspen Plus v10 (extracted from Ref. [42]).

Continuous removal of produced hydrogen from the reactor also influences the equilibrium conversion, favoring higher methane conversion by a selective extraction. Therefore, the utilization of membrane technology can be a promising solution, where membrane act as a barrier to methane so that only hydrogen would be permeated [32]. The integration of membrane separation technologies with conventional methane decomposition reactors offers a promising alternative to conventional separation processes like pressure swing adsorption (PSA), since it enables the production of high-purity hydrogen while avoiding the complexity and high costs associated with PSA [43]. Palladium membranes are commonly used for hydrogen purification and fuel cells applications, becoming a studied possibility on CDM processes [44]; despite being a very efficient hydrogen selective material, the high price cost associated with Pd, its fragility and stability at high temperatures are the main drawbacks [45]. Other interesting possibility that is being addressed in the 112CO2 project is the hydrogen pumping using proton conducting ceramics (PCC) membranes, a technique where a direct current is utilized to form hydrogen protons, which can go through the membrane [46].

Other important aspects are the residence time in the reactor and the contact time between the methane molecule and the catalyst active sites, which consequently affects the final conversion. By decreasing the feed flow rate, the residence time is increased, which enhances the reagent-catalyst interaction. However, below a particular optimum this would also lead to a lower hydrogen production [47]. On the other hand, a higher flow rate has a huge impact in the mass and heat transfer limitations inside the reactor, since the initial conversion would be higher than the diffusion rate and, consequently, the generated carbon would suffer from transport limitation, laying over the catalyst and not diffusing through it [48].

2.1.3 Reaction Catalysts

As previously mentioned, methane molecule is highly stable due to its strong C-H bond and geometric structure. Therefore, the decomposition in the absence of catalyst needs a higher

temperature to occur. The catalyst promotes the reaction by reducing its activation energy, reaching high yields and conversion levels at moderate temperatures. A suitable catalyst for methane cracking must simultaneously present a high activity and stability, resisting deactivation due to carbon accumulation. Over the last decades, enormous efforts have been made to develop an efficient catalyst for CMD. The most relevant ones are metal or carbon-based materials. Even with different catalysts, the reaction mechanism is similar and dependent on the chemical composition, morphological structure and physical interactions of the catalyst. Figure 5 summarizes the most used catalysts for CMD based on their favorable temperature range and produced carbon products [49].

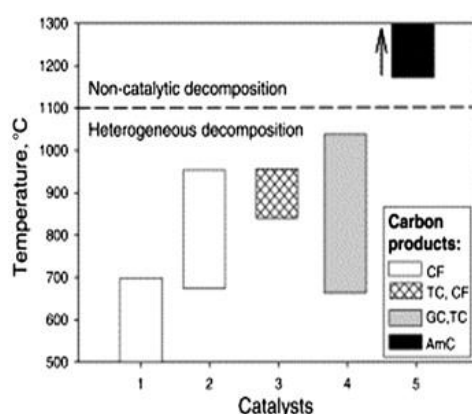


Figure 5 - Methane decomposition behavior with temperature range, and carbon products and catalysts. Catalysts: 1–Ni-based, 2–Fe-based, 3–carbon-based, 4–summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5–non-catalytic decomposition. Carbon products: CF–carbon filaments, TC–turbostratic carbon, GC–graphitic carbon, AmC–amorphous carbon (extracted from Ref. [49]).

Researchers have recently been increasingly interested in thin film catalysts due to their unique properties. Metal thin films such as nickel, cobalt and iron have been reported, being a promising alternative [21]. The high surface area to volume ratio can improve heat and mass transfer rates, leading to enhanced reaction kinetics and efficiency [22]. Besides that, the use of thin films requires less material than traditional bulk catalysts. Overall, the use of thin film catalytic layers holds great potential for advancing the efficiency of CMD.

2.1.3.1 Metal Catalysts

Usually the metal-based catalyst utilized for CMD reaction are composed by an active metal and a support. As active material, various metal catalysts were used, however transition metals, as Fe, Co and Ni, are responsible for the best results so far, mainly due to their high conversion levels and elevated capacity to diffuse the generated carbon through them. Their partially filled 3d orbitals provides special electronics properties, which essentially are responsible for accepting and releasing the electrons of the adsorbed methane, which, consequently, weaken the strength of C-H bonds [34, 35]. Among the previously mentioned metals, iron is the cheapest one. Additionally, it has high diffusion capacity and shows good

results at high temperatures - above 700 °C [34, 50]. However, although being cheap, its application is not a consensus, since higher hydrogen and carbon yields are achieved by other metals [34, 35]. Even so, due to its resistance to deactivation at high temperature, its low price and the production of high market value carbon, iron is a relevant alternative for industrial use [26, 49]. Cobalt represents another option but is rarely used for CMD reaction due to the high price, toxicity, and association with conflict-mineral concerns [34, 50, 51]. The production of valuable CNTs and possibility to operate at high temperature are the main advantages of this metal [52]. Still, nickel is the most investigated catalytic component. Ni is an easily available metal and presents a cost-effective performance on CDM reaction, showing better results than the other metals, *i.e.*, higher activity and conversion levels, producing the highest hydrogen and carbon yields [26]. Besides that, when utilizing Ni, the operation temperature can be reduced to the range of 500-650 °C, which allows a greater energy efficiency. Nevertheless, at temperatures above 650°C, Ni-based catalysts are gradually deactivated due to sintering/agglomeration and the formation of encapsulated carbon over the catalyst surface area [15, 50]. Therefore, for low temperature CMD, the focus of this work, nickel is the most suitable catalyst.

The addition of dopants, such as Cu, Fe, Pd, and Pt, to form an alloy, can enhance the performance and stability of the catalyst. This improves the dispersion of the active metal and influences the carbon growth mechanism, potentially facilitating diffusion over the catalyst and preventing carbon accumulation on its surface [53-55]. However, the high costs and limited availability of noble metals make them unsuitable for industrial operations [55]. Wang *et al.* [20] studied the impact of additives on Ni/Al₂O₃ performance, namely 5 wt.% M-60 wt.% Ni/Al₂O₃ catalysts (M = Cu, Mn, Pd, Co, Zn, Fe, Mg). The reaction was carried out at 650°C and it was observed that all the metals improved the catalyst activity and lifetime. Besides that, it was observed that the secondary metal enhanced the reducibility of NiO, shifted the optimum temperature and lowered the deactivation rate, mainly by moderating the activity and improving the rate of carbon diffusion through the catalyst.

The support plays an essential role in the catalytic reaction, mainly due to the physicochemical interactions between the support and the metal layer. Inorganic oxides supports, such as Al₂O₃, SiO₂, TiO₂, MgO, CaO and zeolites, are frequently utilized as inert support for the CMD [56]. The main function of the support is to improve the metal dispersion over its high surface area and porosity, allowing a high metal loading and an equal distribution of the active metal [50]. A MSI provides better attachment and dispersion to the metal, increasing the sintering resistance by reducing the metal mobility and promoting changes on the crystallinity and surface electronics [15, 35]. Moreover, a suitable MSI prevents the formation of unwanted large particles or agglomerations. However, when the MSI is too strong,

it tends to form structures that are difficult to reduce and more intense reduction processes are necessary [34]. The support nature also enhances the diffusion behavior, increasing the catalyst activity and preventing the deactivation. The morphology, texture and crystallinity are essential aspects related to the catalytic results. Awadallah *et al.* [19] studied the effect of crystalline structure and pore geometry of silica supported Ni catalyst during the CMD reaction, showing that the performance is strongly dependent on the support characteristics. In addition, the support nature also influences the type of the generated carbon nanomaterial. Due to its large surface area and suitable pore size distribution, Al_2O_3 is one of the most recommended supports [6, 20]. Supported catalysts have several advantages over unsupported catalysts for methane decomposition, as shown in the comparison between dip-coated catalytic layers of unsupported nickel and $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ done on [57]. The supported Ni sample demonstrated higher hydrogen productivity and stability, with continuous production lasting over 30 hours. The reaction was stopped prior to excessive deactivation occurring.

Particle size is another extremely important factor for CMD, which is strictly dependent on the catalyst composition and reaction conditions. A smaller particle size typically leads to a larger surface area, However, a higher tendency for particle agglomeration and sintering is also observed, which is prejudicial for the catalyst stability [58]. Besides that, among all catalyst properties that affect carbon formation, the particle size is one of the most crucial factors. Xu *et al.* [59] investigated the effect of Ni particle size on the carbon by-product selectivity for $\text{Ni/Al}_2\text{O}_3$ and $\text{Ni/MgAl}_2\text{O}_4$ catalysts. It was observed that large Ni particles (>20 nm) are selective toward the formation of CNTs, while small Ni particles (<10 nm) are selective towards the formation of graphitic carbon layers. Additionally, the optimal particle size changes with the operation temperature. Pinilla *et al.* [60] studied the catalytic activity of Ni supported on Al_2O_3 and MgO with crystalline sizes ranging from 10-80 nm at 500-700 °C. In general, Ni crystal sizes of 10-20 nm showed better performance in the studied temperature range. This may be associated with the delicate balance between decomposition rate and carbon diffusion. Table B.1 in Appendix B presents a comparison between Ni catalysts.

2.1.3.2 Carbonaceous Catalysts

The main problem associated with metal catalyst is the gradual deactivation after a high initial activity, which is mainly caused by the deposition of solid carbon over the catalyst surface, blocking the active sites. Carbon catalysts, on the other side, present a higher stability against carbon accumulation - the generated carbon mixes with the catalyst and helps to maintain the reaction rate up to a certain limit [50]. Because of that, they also present a greater stability at high temperatures (above 750 °C) and, depending on the operation condition, no regeneration or separation step is needed [61]. Carbon catalysts are a real possibility for CMD since they are cheaper and more resistant to poisoning than the metals ones

[15, 26, 32]. Among the carbon based catalyst, active carbon and carbon black are the ones that presented the best results and, consequently, are the most promising [50]. However, despite some clear advantages, carbonaceous materials present several limitations that prevent its practical utilization for CMD: the lower conversion levels and H_2 yield compared to metals catalysts are the main drawbacks [26, 50]. Furthermore, the difficulty of regenerating the catalysts without damaging them restricts their suitability for long-term operations compared to metal catalysts [15].

2.1.4 Reactor Design

The reactor design plays a critical role in methane decomposition reaction. Several reactor configurations, such as fixed bed reactor (FBR), fluidized bed reactor (FLBR), plasma bed reactor (PBR) and molten metal reactor (MMR), have been studied in order to obtain the most stable and cost-effective option. Material selection is also important, impacting stability and capital costs of the methane decomposition reaction. The selected material should be non-corrosive, inert during the reaction, easily available, and non-expensive. For high temperature processes, such as methane decomposition on plasma reactors, materials with exceptional thermal and mechanical properties are necessary. Tungsten, titanium and quartz are examples of highly stable materials at high temperatures ($>900\text{ }^{\circ}\text{C}$) and harsh chemical environments, mainly due to their high melting point, strength, and low thermal expansion coefficient. However, they are difficult to handle and expensive. For low temperature processes ($<700\text{ }^{\circ}\text{C}$), which is the focus of this research, a contactor reactor is the most suitable design; this temperature allows the use of materials such stainless steel (SS), a cheaper and more viable alternative. In this temperature range, iron alloys are stable and not catalytically active. SS310, SS316 and ferritic SS are examples of different types of SS that can be applied.

FBR reactors are usually used on laboratorial scale to analyze the different catalyst activities and the effect of experimental parameters, such as the feed flow, partial pressures of components, regeneration cycles and temperature [6, 26]. However, the main drawback of fixed bed reactors is the poor mass and heat transfer, which can eventually lead to pressure buildup inside the reactor and even blockage due to carbon accumulation [15, 50]. An alternative to avoid such problems is the utilization of FLBR, which can maintain the operation for longer periods and prevent the reactor clogging. On fluidized bed reactors, the generated carbon and deactivated catalyst can be continuously removed from the reactor, while new catalyst is loaded, allowing the reaction to continue without interruption [15, 50]. However, the constant utilization of new catalyst represents a costly option, thus regeneration cycles are a cheaper alternative. Besides a lower pressure drop, better mixing and maximization of heat and mass transfer due to fluidization, achieving longer operation periods is still a challenge, mainly due to carbon accumulation [15, 50]. Due to the previously cited limitations, both

configurations do not achieve high operation lifetimes, being utilized for batch production of carbon structures through CMD since the middle of 20th century [28].

On the other hand, PBR and MMR are examples of promising options but energy intensive reactors layouts. On PBR, high temperature from the plasma arc is responsible for methane cracking. A large voltage is needed to produce the plasma and, consequently, the high electricity demand is one of the major obstacles of this technology [26, 28]. Moreover, the potential formation of unwanted by-products, mainly heavier hydrocarbons, and the carbon accumulation on the electrodes also represent a complication [15]. Despite presenting advantages, as the possibility to operate without catalyst, high initial cost and safety conditions make this technology difficult to scale-up. In contrast, MMR represents an interesting approach since the catalyst deactivation due to coking is prevented. The working principle of MMR is relatively simple: methane is fed into the bottom of the reactor, and the catalytic reaction takes place at the interface between the liquid metal and the gas bubbles. The produced carbon floats and can be easily collected at the top of the reactor, due to its lower density compared to the molten metal [26, 28]. The easy separation of the formed carbon and high heat transfer among the gas-liquid medium are the main advantages of this technique. Figure A.4 and A.5 illustrate PBR and MMR operation, respectively. Both configurations can achieve higher operations lifetimes than fixed bed and fluidized reactors. However, the high temperature needed, near to non-catalytic decomposition, and possible corrosion of the reactor material are severe problems that need to be solve prior to industrialization [15, 50]. To fulfill the high energy demanded for these processes, the adoption of renewable electricity as energy supply, such as concentrated solar reactor power systems, can be an option and is currently being studied [62].

Likewise, as mentioned before, association of membrane technology is also a promising approach to enhance the efficiency and ensure a pure hydrogen stream. A catalytic contactor reactor consists of a catalytic placed bed in series with a substrate module [63]. In a thin film catalytic contactor reactor, a thin catalytic layer is coated on the substrate surface. The reactants then flow over the catalytic film, where the reaction occurs, and in combination with membrane technology, the products selectively permeate through the substrate. This allows for favorable product generation through equilibrium, retention of unreacted reagents inside the reactor, and the generation of an outflow rich in the desired product [63]. This phenomenon offers various advantages in terms of product selectivity and control. The substrate system operates based on three main principles: (1) size exclusion, (2) adsorption and (3) electrostatic repulsion/conduction [63]. Contactor reactors for methane decomposition are currently in a development stage, however, very few articles are found about this configuration in the literature. Han *et al.* [64] tested the efficiency of a $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_3$ ceramic membrane covered

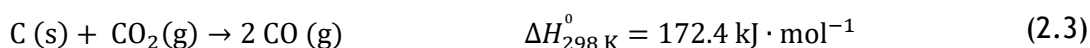
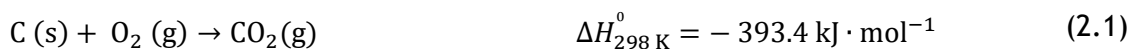
with a 50 nm thick Pd catalytic film at 600, 700 and 800 °C, achieving a 48.3 % conversion and presenting a stable operation for more than 300 min without regeneration. The Pd layer and tested operation temperatures were responsible for the methane molecule adsorption and decomposition into the hydrogen molecules. They suggest that the Pd layer is also responsible for the dissociative adsorption of the H₂ molecules. Consequently, the proton is transported through the mixed conducting membrane, being desorbed on the other side of the surface, and associated with the electron to form again the hydrogen molecule. The suggested membrane presented a high total electrical conductivity, making unnecessary the use of an external electrical circuit.

2.1.5 Deactivation and regeneration

Catalysts used for chemical processes do not present a constant performance and gradually lose activity due to several factors. The most common causes of deactivation are poisoning, coke accumulation and sintering [65]. Natural gas, the main source of methane for CMD at industrial level, contains small amounts of harmful compounds to the catalyst, namely sulfur species. The catalyst poisoning occurs due to the formation of metal sulfides on the catalyst surface, which inhibit the access of methane molecule to the metal active site, preventing its adsorption [65]. Sintering usually happens at high temperatures and it is an irreversible deactivation process. During this phenomenon, small metal particles merge and originate larger particles, which results on a loss of activity by the reduction of the catalyst surface area, limiting the exposure of the active site to the reactant [15, 35, 65]. Carbon deposition, as previously explained, cannot be avoided as carbon is one of the products of the decomposition reaction, leading to surface coverage catalyst encapsulation and, consequently, deactivation.

Several strategies are employed to prevent the catalyst deactivation and prolong its lifetime. The poisoning phenomenon can be avoided by doping the catalyst with other metals, which are responsible for protecting the active sites in charge of the decomposition [65]. Furthermore, an additional purification step to generate pure methane without contaminants can also be applied. The use of a strong MSI can effectively prevent sintering by securely anchoring the metal particles onto the support surface. However, this approach can introduce some drawbacks, such as increased complexity in the reduction process [15, 35, 65]. Regarding carbon removal, separation and regeneration techniques can be employed. Separation methods are simple but not fully efficient, since they do not totally remove the carbon particles inside the catalyst structure [33]. On the other side, the adoption of regeneration processes is an alternative to maintain a continuous operation by gasifying the carbon deposits. Regeneration theoretically enables the process to continue indefinitely as long as the carbon deposits over the catalyst via base-growth. However, if the carbon grows between the catalyst and support through tip-growth, regeneration becomes impossible and permanent loss occurs. Combustion

and gasification, with steam of carbon dioxide, are examples of catalyst regeneration processes and are illustrated by the equations (2), (3) and (4), respectively [15, 32, 33]. These gases are responsible for removing parts of the carbon, allowing the catalyst surface to be exposed and active again.



Through the adoption of these regeneration processes, an operation without any significant loss of catalytic activity over several cycles is possible. However, the main disadvantage of these regeneration processes is the formation of GHG, causing direct emission of pollutants similar to other processes and nullifying the ecological perspective of methane decomposition. Moreover, an additional purification step would be necessary to produce clean hydrogen. Other major drawback of the regeneration process is that the generated carbon is destroyed, preventing the economic valuation of these nanomaterials [50]. In the case of gasification with steam and CO₂, an additional water-gas-shift reaction can be employed to produce more H₂. Mendes *et al.* [16] proposed a cyclic regeneration process with a small fraction of the produced hydrogen, shifting the equilibrium towards methane formation, which leads to a reduction in the carbon accumulation and, consequently, restoring the catalyst initial activity without GHG emissions. This innovative approach in combination with the utilization of thin films catalytic layers on contactor reactors can be an interesting alternative to the current established technologies for CMD.

2.2 Screen Printing

Screen printing is a common deposition technique utilized for coating of catalytic thin films onto a substrate surface. In accordance with the application/objective, several techniques can be utilized for deposition of material and fabrication of thin films. Ukoba *et al.* [66] divided it in three groups: (1) physical vapor processes, as pulsed laser deposition; (2) chemical vapor processes, as chemical vapor deposition and atomic layer deposition; (3) chemical solution processes, as dip coating, spraying and screen printing. However, among all methods, screen printing is one of the most simple, flexible, cheap, and scalable technique; it is widely used on the fabrication of solid oxide fuel cells (SOFC), photovoltaic cells and even electronic devices, like circuit boards and micro-sensors, efficiently printing films with a thickness in the range of 10-100 μm [67]. Besides these advantages, this technique also offers a good adaptability/suitability for a wide range of substrates and an easy incorporation of catalysts by simply adding them to the paste formulation [68]. Figure 6 presents the main components of the screen printing process. The sequential operation steps are: (1) the pre-printing step, where

the viscosity is high and the ink is relaxed; (2) the printing step, where squeegee applies a tangential stress on the paste, breaking the rheological structure and, consequently, the viscosity is drastically reduced, which allows the passage of the paste through the aperture of the screen mesh; and (3) the post-printing step, where the paste should recover its initial structure as fast as possible after the deposition on the substrate to avoid bleeding and maintain the printed pattern [67, 68].

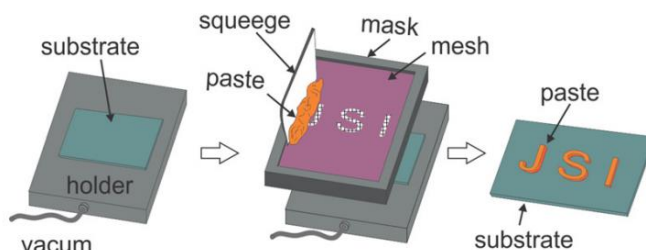


Figure 6 - Schematic representation of the screen printing process (extracted from Ref. [23]).

Unlike other processes, such as spraying, the pastes utilized for screen printing should have a higher viscosity and a thixotropic behavior, *i.e.* a decrease in viscosity at a constant shear rate [69]. Because of that, the composition and formulation of the paste is a fundamental aspect. The pastes are usually composed by a catalytic powder, an organic solvent, a binder, and a dispersant. The fraction of each component needs to be carefully selected. Additionally, adjusting parameters of the printer itself can drastically affect the quality and thickness of the films. The mixing process also has a critical role by breaking down the particle aggregates and producing a homogeneous paste. Likewise, drying the wet film is a crucial step, since it involves uncountable phenomena, from particle dynamics to mass and heat transfer, drastically affecting the final morphology of the printed film and the adhesion to the substrate. Consequently, a deep understanding of each area is vital to manufacture a proper film [70].

For the first time, Ni thin layers for CMD are deposited by screen printing technique; dip-coating and PVD are examples of techniques normally reported [71, 72]. The target is to produce a film as thin as possible, capable of being extremely reactive while using a small quantity of material. As previously mentioned, thin films have unique properties, namely the high surface area to volume ratio. Thicker layers must be avoided since it would decrease the amount of exposed active sites of nickel particles, being prejudicial to the performance. Therefore, the application of screen printing deposition technique will be used and adapted to produce Ni-based catalytic films on substrates for methane decomposition reactors.

2.2.1 Components of the paste

The paste needs to be stable and homogeneous to provide a good printability and uniformity. It is mainly composed by an active material, usually a catalytic powder, and a solvent, responsible for the suspension of the powder and formation of a homogeneous mixture. However, phenomena like sedimentation (when the gravity force overcomes Brownian motion)

and agglomeration (mainly due to Van der Waals forces) are extremely common, resulting in a problem to the printability. To avoid this situation, a dispersant can be introduced to establish a repulsive force between the particles, either by charge difference (electrostatic stabilization), reduction of the particle interaction (steric stabilization) or both at the same time (electrosteric stabilization) [23]. Binders are other possible additives used to improve the particle network, preventing the formation of defects and enhancing the adhesion onto the substrate by bridging the particles. The balance between these components generates a series of interaction and forces, such as Brownian force, hydrodynamic and interparticle interactions, responsible for the physicochemical characteristics of the paste. However, the addition of these components severely changes the printability by altering its rheological nature (the binder makes the paste more viscous, while the dispersant has the opposite effect). Therefore, a complete analysis to find the optimum composition of the paste is indispensable.

The powder characteristics are directly related to the maximum acceptable loading; particle size, superficial area and distribution of the powder have a huge impact on the solid content and the rheological properties of the paste. Powders composed by nano-sized particles consequently presents a high surface area, which increases the interparticle interaction, making the paste highly viscous even at low solid content (>40 wt.%) [67, 73]. The utilization of a paste with low solid content also increases the possibility of cracking during the drying step, due to reduced wet film density and increased film shrinkage during the drying. Sung *et al.* [74] investigated pastes with two different sizes of Ni particles (average diameters of 120 nm and 180 nm). Through rheological and morphological tests, it was detected that the paste prepared with smaller particles presents a greater viscosity and pseudoplastic nature due to the stronger network structure; the ball milling process has a huge importance on the paste composition and rheology, since it reduces the particle sizes. According to previous studies, the particles should have a narrow distribution in the range of 0.1 μm - 10 μm [75]. Aside from the size, by just increasing the solid content, the paste increases its viscosity and elastic properties, which can also be explained by the greater particle association.

The solvent's function is mainly to disperse dry components, forming a uniform and homogeneous paste. Solvent properties, as type (organic or inorganic), boiling point and viscosity, directly affect the paste composition and the final structure of the deposited film. The type is a crucial factor in terms of rheological properties and activity because it impacts the maximum solid content of the paste, while the boiling point and viscosity affect the final morphology of the catalytic layer, mainly by influencing its drying properties [68, 73]. Another important aspect is the solvent dielectric constant, which impacts the stability and relation with the catalyst, dictating the formation of a dispersion, a colloid or a precipitate, *i.e.* the catalyst dispersion on the solvent [73]. According to Bonifacio *et al.* [76], the solvent, being

responsible for surround the solid, is the first paste component to come in contact with the substrate. Therefore, the paste surface tension is mainly determined by the solvent used, which must be lower than the substrate to avoid adhesion problems and coating failures. The choice is directly dependent on these properties and the deposition method. In the case of screen printing, low viscosity and volatile solvents, such as water, ethanol and isopropanol, are not recommended, because they dry off relatively quickly, resulting in a poor distribution and storage instability. Also, the paste usually acquires a liquid-like property, leading to slumping and bleeding during the printing [67]. The most commonly used solvents for screen printing are non-volatile alcohols with moderate chain, such as terpineol and texanol, but the utilization of other compounds, like propylene glycol and cyclohexanol, and even mixtures of them is also a possibility [73, 77].

The binder is a possible additive compound that could improve the particle network strength, and is usually used in a low quantity (0-5 wt.%). Generally is a non-volatile polymeric compound that adsorb onto the particle and controls the rheological behavior of the paste, providing an optimum shear-thinning pseudoplasticity and a suitable adhesion on the substrate [77, 78]. On ceramic substrates, the binder interacts with the solid through hydrogen bonding between the binder hydrogenated groups and the surface oxygen of the ceramic components [79]. The absence of binder can cause poor thixotropic behavior and, consequently, make the paste not suitable for screen printing; this is mainly due to the weak inner network strength without the hydrogen bonding [80]. The deposition of pastes with low binder may result on film cracking during the drying due to the reduced particle strength [67]. On the other hand, high binder content increases the viscosity and limits the maximum solid content, which hinder the catalyst activity [67]. Some common binders utilized in screen printing applications are ethyl cellulose, polyvinyl butyral and polyvinyl acetal. However, the use of organic binders are generally not suitable for high temperature processes, since they can decompose or burn, leading to a loss of adhesion and structural stability [23, 77]. In contrast, inorganic binders, such as glass frits and aluminum/silicates-based compounds, are better suited for high temperature processes, as they can withstand higher temperatures without breaking down [81, 82]. The solvent-binder interaction is a key aspect on the paste formulation, because if the particle dispersion is low, the bridging will be reduced [80]. Therefore, the binder selection and content optimization are essential to produce a high-quality paste and crack-free film.

Particle sedimentation and agglomeration are undesired phenomena that reduce the paste quality. The dispersant's role is to enhance the segregation of the solid particles, acting in opposition to the gravity and the Van der Waals attractive forces [23, 67, 73]. Hence, the generation of repulsion forces, either through particle electrical charging or the formation of a steric barrier (polymeric layer adsorption that physically hinders particle approximation), is essential for achieving a homogeneous and well-dispersed paste [23, 83]. As result of this

effect, the dispersion is enhanced and, consequently, the particle interaction and paste viscosity are reduced, allowing an increase of the maximum solid content of the paste [67]. Compounds with different polarities and structures are selected in accordance with the other components of the paste. The dispersant quantity usually is recommended by the supplier, being directly proportional to the solid mass and particle surface area [67, 73].

2.2.2 Screen printer parameters

To produce high quality films and improve the efficiency of deposition, parameters such as squeegee load, squeegee velocity, squeegee type, squeegee angle, mesh type, substrate type, and snap-off distance (adjustable distance between the substrate and screen) must be analyzed and optimized [67, 68]. Figure 7 presents some of the most important parameters. These parameters can be adjusted in accordance with the paste rheology, adapting to its viscosity and having the same importance as the composition to achieve the desire pattern and thickness. However, the relationship between the resulting film and these parameters has received limited attention from researchers. Nevertheless, some general recommendations have been proposed, such as increasing squeegee pressure and reducing velocity, especially when the paste exhibits high solid-like behavior [84]. Also, to produce uniform thin films, the squeegee load and squeegee hardness can be increased, while the squeegee velocity and snap-off distance should be reduced [67].

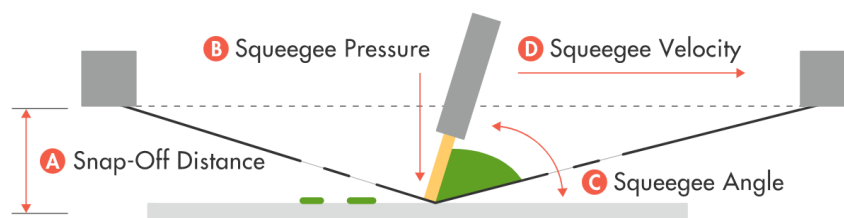


Figure 7 - Schematic representation of some screen printing parameters (extracted from Ref. [85]).

Somalu *et al.* [86] succeeded in fabricating a Ni/ScSZ electrode for SOFC with a thickness of 10 μm . The composition of the used paste was modified to observe the influence on the rheological behavior, while keeping a reasonable highly viscous profile (ca. around 1000-4000 Pa·s at 0.1 shear rate). However, parameters as squeegee load, squeegee velocity and snap-off distance remained constant (6 kg, 20 $\text{mm}\cdot\text{s}^{-1}$ and 2 mm, respectively) and the thickness barely changed, suggesting that the film thickness can be adjusted by manipulating the screen printer parameters. Nonetheless, these parameters must be defined by observing the paste comportment during the printing process. Hung Lee *et al.* [87] studied the effect of other parameters on the morphology of printed electronic devices. Specifically, the number of printing cycles and the screen mesh size were examined to understand their influence on resistance and conductivity. The results indicated that increasing the mesh density and the number of cycles led to lower resistance and higher conductivity. However, it was also found that higher number of cycles and a denser mesh made the printed pattern present a smoother

topography with fewer voids. The number of cycles directly affect the surface flatness, since the additional paste can fill the previously formed voids, creating a more homogeneous surface. Moreover, the mesh material is also an important aspect. Usually polymeric and metal materials are utilized to fabricate the mesh. However, they present completely different properties, like flexibility, resistance and even chemical interaction with the paste [68].

2.2.3 Other parameters

The substrate properties have a significant impact on the final microstructure and morphology on thin films deposition processes. For CMD, the substrate should be inert during the reaction and must be resistant to high temperature, maintaining its characteristics, as hardness and flexibility, regardless of the environment. The texture and porosity of the substrate will hardly influence the catalytic layer by altering the adsorption phenomenon and its velocity [88]. A porous surface also affects the mass transfer during the reaction, which can enhance the transfer phenomena or even be a problem due to passage block by the generated carbon. Besides that, the substrate material is an important aspect since it affects the interactions with the catalyst and, consequently, the coating adhesion. Due to the high temperature, ceramic and metal materials are possible substrate materials for CMD. To enhance the adhesion and improve the coating, the material can go through a series of treatments. Acidic chemical treatment and anodic oxidation are examples of well-known surface pre-treatment to improve the attachment and quality of the thin-film layer.

The quality of the screen printed film is also dependent on the final drying step. The removal of the organic compounds, such as the solvent evaporation and binder burnout, if present, has a strong impact on the final microstructure of the catalytic layer. The drying rate involves several phenomena, including mass and heat transfer as well as interparticle forces. These factors directly affect the structure of the dried film, consequently influencing properties such as porosity and catalyst dispersion [23, 70]. The drying phenomenon can be divided into two stages: (1) film shrinkage occurs due to the evaporation of most of the solvent; (2) the remaining solvent is evaporated and only a small change in thickness is observed, causing a porous network among the particles [70]. If the drying occurs too fast, at high temperatures, there is a greater chance of cracking and defects. However if it takes too long, a possible phase separation can happen, losing the original wet film pattern [23]. Talukdar *et al.* [89] studied the effect of different drying methods, namely common oven drying, vacuum drying and freeze drying, on the fabrication of an electrode catalytic layer. It was observed that the pore volume and pore size distribution is strongly dependent on the drying technique. The freeze-dried sample presented increased porosity and surface area compared to the other samples. However, it also exhibited higher thickness. In contrast, the traditional oven drying method resulted in poor porosity and the lowest thickness among all samples.

3 Materials and Methods

The materials and methods section contains information about the preparation and composition of the Ni-based paste, screen printing parameters, drying treatment of the printed films and procedure of the comparative method, *i.e.*, wet spray. Besides that, the CMD setup and the methods adopted to characterize the catalytic layer are also mentioned.

3.1 Experimental procedure

3.1.1 Catalytic paste formulation and deposition through screen printing

A commercial Ni/SiO₂-Al₂O₃ powder (Ni 65 wt.% loading - purchased from Sigma Aldrich, serial number: 208779-100G) was utilized to produce the paste. Propane-1,2-diol (≥ 99 % purity - purchased from VWR Chemicals, serial number: 432628) was utilized as organic vehicle. α -Terpineol (≥ 90 % purity - purchased from Sigma Aldrich, serial number: 24414.296) was also tested, however presented stability issues due to the low melting point. Appendix C compiles information about the used solvents. Initially, since the objective was to analyze screen printing as deposition method for preparing a thin film, a paste composed only by the catalyst and solvent was considered. Different solid contents were tested to find the best paste composition, in particular 60 %, 65 % and 70 %. The mixture containing the catalyst and solvent was previously hand-mixed and then taken to the ball mill (Planetary Ball Mill PM-100, Retsch). The production of a homogeneous paste, without agglomerates, is essential and, consequently, the milling process had a huge impact on the particle size, which is directly related to the paste rheology. All the pastes went through a sequential milling process: 1 h at 300 rpm, 1 h at 200 rpm and 1 h at 400 rpm. The milling process was performed on a zirconia container containing three zirconia balls. For the production of the paste, each batch contained 5-8 g of catalyst to avoid excessive milling and losses due to adhesion to the container walls. Between each stage, rheological tests were made to study the paste properties. A small amount of the paste was also collected and the solvent was evaporated in order to perform a granulometric test. The following nomenclature was proposed for the prepared pastes: T-SC, where T is the time that the powder was subjected to the milling process (1, 2 or 3 h) and SC is the solid content (60, 65 or 70 wt.%).

Once the best composition was found and the paste prepared, the coating can be done. An AT-45 PA screen printer, purchased from ATMA, was used to apply a 1.5 cm diameter Ni/SiO₂-Al₂O₃ coating on top of a planar substrate. The paste preparation and coating were performed on the same day; the screen printing process was performed at room conditions. Briefly, in a screen printing process, a spreader is responsible for spreading the paste on the opening, and the squeegee to apply a force against the opening, making the paste pass through the mesh and reach onto the substrate. The squeegee was powered by a relative pressure of

2 bar. During this stage, the wet film thickness can be controlled by altering the snap-off distance; the distances of 0.8, 1.0, 1.2, 1.5 and 1.8 mm were tested. Besides that, the velocity and squeegee angle were set at $50 \text{ mm} \cdot \text{s}^{-1}$ and 15° . Planar glass substrates were selected as substrate to analyze paste adhesion and quality of the printed film. Before the coating, the substrates were cleaned with ethanol on an ultrasonic bath for 1 h. After the coating, the samples were dried on an oven. The oven was heated for 3 h to 200°C , held at that temperature for 8 h, and then cooled to room temperature. This process is responsible for removing the solvent, establishing the final structure of the film. The sample was weighed before and after the drying process to verify the catalyst deposition amount. After the drying process, the sample was ready to be tested. These samples were identified as SP-D, where SP indicates that the substrate was coated by screen printing method and D is the snap-off distance. The screen printing setup and the obtained substrates are shown in Figure 8.

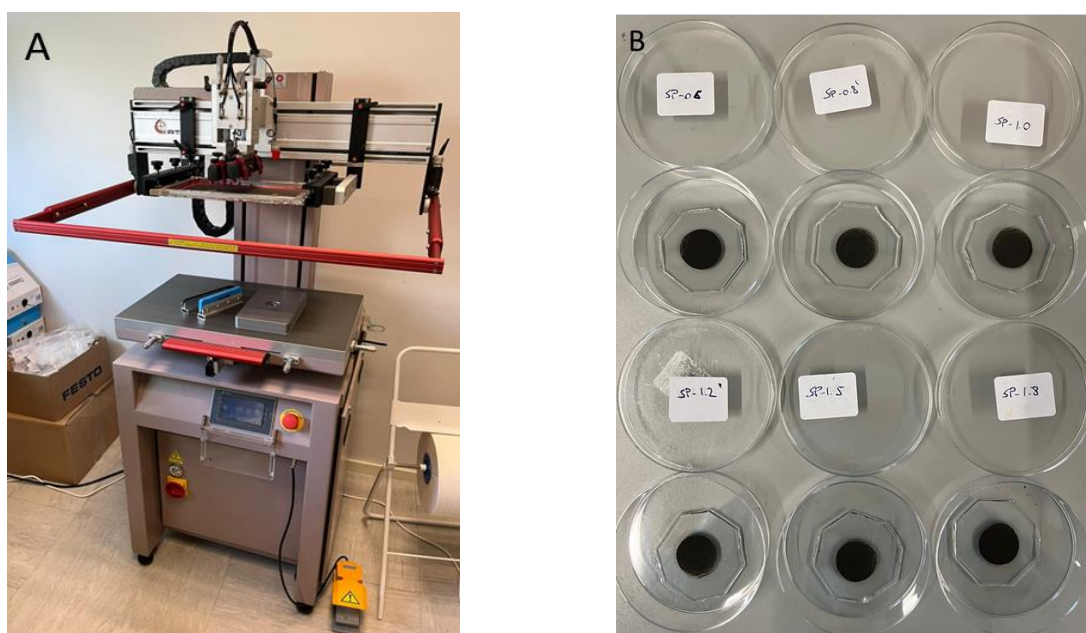


Figure 8 - Screen printing setup (A); Screen printed substrates and their respective identification at the top (B).

3.1.2 Wet Spray deposition

Wet spray is a simple and versatile technique widely applied for the production of thin films with high-density packaging and high uniformity of particles [66, 90]. During this process, the catalytic powder is mixed in a liquid vehicle, forming a homogeneous dispersion. This dispersion is then atomized into fine droplets that are sprayed towards the substrate. The substrate is heated to an appropriate temperature, leading to a quick evaporation of the solvent as the droplets come in contact with the hot surface. The thermal decomposition of the liquid carrier results in the formation of the catalytic layer. The wet spray, despite its simple principle, is hugely affected by the atomizing pressure, solution concentration, and gap between the substrate and spray gun. Figure A.6 presents a schematic operation diagram.

During the wet spray method, a dispersion containing the same Ni/SiO₂-Al₂O₃ powder, water and propane-2-ol ($\geq 99.5\%$ purity - purchased from Honeywell Chemicals, serial number: 190764) was prepared. Unlike screen printing, wet spray solvents must present low viscosity and low boiling point (Appendix C compiles information about the used solvents). The catalytic powder used to compose this solution was the powder derived from the 3-60 paste. This powder was selected due to the particle size in the nanometer range. During this process, a $5 \text{ mg}_{\text{cat}} \cdot \text{mL}^{-1}$ solution with equal quantities of water and propane-2-ol was placed under an ultrasonic bath to promote homogeneity and avoid sedimentation. Glass was also chosen as substrate. During the process, the substrate is placed on a vacuum bed and heated up to 115°C . The solution is placed on a reservoir and sequentially deposited onto the substrate with a spray gun. Due to the high temperature, the solvent quickly evaporates. The configuration setup and operational parameters were previously optimized by LEPABE team. Four substrates were coated simultaneously with a 2 cm diameter. An atomizing pressure of 1.2 bar was utilized. The samples prepared by wet spray are coded as Spray-x, where x is the sample loading ($\text{mg}_{\text{cat}} \cdot \text{cm}^{-2}$). Figure 9 presents the utilized wet spray setup and the obtained substrate.

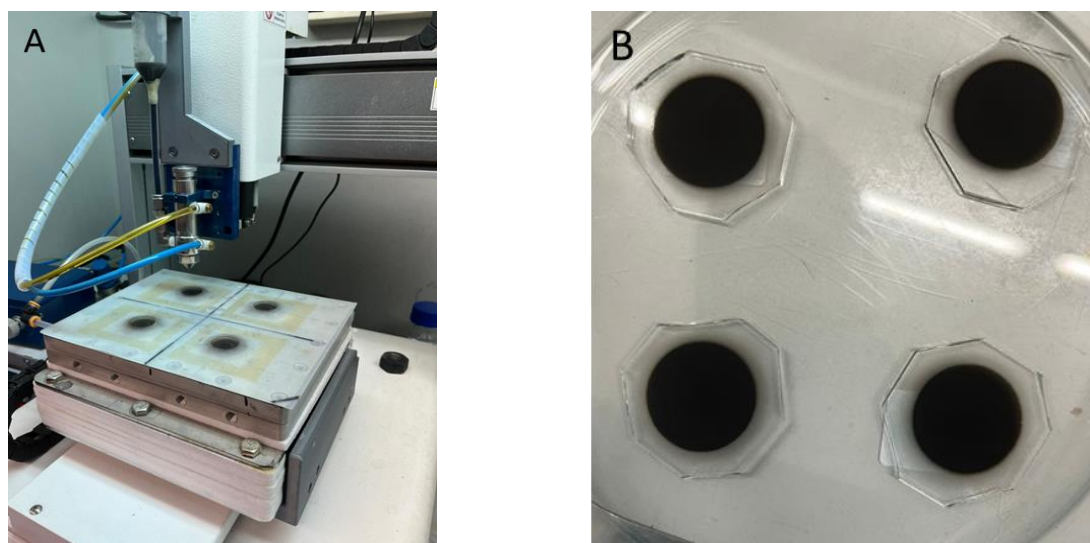


Figure 9 - Wet spray setup (A); Sprayed substrates (B).

3.1.3 Reactional CMD setup

The tests were carried out on a planar cell contactor reactor. The reactor is composed by two-chambers and the substrate is placed in the middle with the coated side facing the bottom. A vermiculite interlayer is utilized as sealant. The reactor is made of steel and sealed with six torque screws. After the sealing, a leakage test is performed, where a maximum pressure loss of $30 \text{ mbar} \cdot \text{min}^{-1}$ is allowed. Methane and argon are fed at the bottom of the reactor, while hydrogen is fed on the top. Furthermore, the reactor presents an extra volume due to carbon growth and accumulation. Initially, the reactor was heated up to 550°C with a temperature rise of $1^\circ \text{C} \cdot \text{min}^{-1}$ while Ar, an inert gas, is fed at a constant $10 \text{ mL} \cdot \text{min}^{-1}$ rate. All the operation is carried out at 1 bar. Initially, to understand the catalytic film behavior, a continuous

decomposition process was performed. Due to time limitations, it was not possible to operate until the catalysts were completely deactivated. An additional regeneration process was performed accordingly to [16], involving cyclic decomposition and regeneration operation. Gas fraction results were obtained in a 3 min interval through a gas chromatography (GC) equipment, Nexis GC-2030, purchased from Shimadzu Corporation. The confidentiality of operational information, including the reactor design and the specific flow rates employed, is maintained.

3.2 Physicochemical analysis methods

3.2.1 Rheological tests

Two rheological analyses were performed to analyze the viscosity and thixotropic behavior of the formulated catalytic pastes: a viscosity curve and a three interval thixotropy test (3ITT). All tests were executed on a rotational rheometer (MCR 92, Anton Paar) equipped with a 50 mm diameter lower and upper parallel plates. The gap distance was set on 1 mm. It is essential to do all measurements at a constant temperature since the viscosity is strongly dependent on it. A temperature of 20 °C was chosen for the experiment. The viscosity curve or steady-shear flow experiment was performed at a shear rate range of 0.1-1000 s⁻¹. Additionally, comparing the viscosity of the material at two different shear rates, usually differing by a factor of 10, such as 4 s⁻¹ (low-shear viscosity) and 40 s⁻¹ (high-shear viscosity), allows to numerically measure the pseudoplastic profile. The ratio between the viscosity at 40 s⁻¹ over the viscosity at 4 s⁻¹ is known as thixotropic index [91]. For the pastes with a suitable viscosity (not too viscous and not too liquid), the 3ITT was also performed, aiming to simulate the paste comportment during the screen printing process [91]. During the first 25 s (first interval), the shear rate was 0.5 s⁻¹ to replicate the paste rest behavior on the screen mesh prior to the screen printing. Then a shear rate of 1000 s⁻¹ was applied for 0.6 s, reproducing the squeegee action. In the final interval, the shear rate was returned to its initial value for 150 s to simulate the structure recovering. The time it takes to recover the initial viscosity indicates the regeneration factors of the paste after structure breakdown under high shear conditions.

3.2.2 Laser diffraction

With the aim to analyze the particle size distribution, laser diffraction method was performed on a LS-230 Coulter. The powder was dispersed in water to ensure that the particles were evenly distributed and to prevent agglomeration. This technique relies on the scattering of laser light in different directions when the beam collides with the particle. With the help of a detector, the scattered light is measured and related to the particle size.

3.2.3 Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Through Scanning Electron Microscopy (SEM), the morphology, surface appearance, as well as the layered arrangement and film thickness of the catalytic film was studied. A Hitachi TM4000 plus equipment was used applying a voltage of 15 kV. The analyses were performed before and after running CMD reaction. Energy-dispersive X-ray spectroscopy (EDS) was also performed to verify the atomic composition and distribution on the coating; a XFlash 6-30 from Bruker was utilized.

3.2.4 Reaction performance

The methane conversion (X_{CH_4}) during the decomposition reaction was determined by equation 3.1, where y_i is the molar (volumetric) fraction of component i on the stream. The hydrogen production activity (a_{H_2}) is calculated by equation 3.2, where $\dot{m}_{H_2}$ is the hydrogen produced mass flowrate in $g_{H_2} \cdot h^{-1}$, W is the catalyst mass (Ni phase and support) present on the sample in g_{cat} , F_{H_2} is the produced hydrogen volumetric flow at normal pressure and temperature (NPT) conditions in $mL \cdot min^{-1}$, ρ_{H_2} is hydrogen density at NPT conditions in $g_{H_2} \cdot mL^{-1}$, F_{CH_4} is the inlet methane volumetric flow at NPT conditions in $mL \cdot min^{-1}$, M_{H_2} is the molar mass of hydrogen in $g \cdot mol^{-1}$ and V_m is the molar volume NPT conditions ($22.4 L \cdot mol^{-1}$). In order to standardize the results, the activity is calculated as $g_{H_2} \cdot g_{cat}^{-1} \cdot h^{-1}$. The equations were obtained by assuming ideal gas behavior for all the gases used and normal temperature and pressure conditions.

$$X_{CH_4} = \frac{y_{H_2}}{y_{H_2} + 2 \times y_{CH_4}} \times 100 \quad (3.1)$$

$$a_{H_2} = \frac{\dot{m}_{H_2}}{W} = 60 \frac{F_{H_2} \rho_{H_2}}{W} = 60 \frac{2 \times F_{CH_4} \times X_{CH_4} \times M_{H_2}}{W \times V_m} \quad (3.2)$$

To measure the hydrogen consumption during the regeneration step, the H_2 conversion, X_{H_2} , can be calculated by:

$$X_{H_2} = \frac{2 \times y_{CH_4}}{y_{H_2} + 2 \times y_{CH_4}} \quad (3.3)$$

Other important parameter to analyze the catalyst efficiency is the carbon yield (C_y), which indicates the mass of carbon produced during the reaction per mass of catalyst. Equation 3.4 describes the calculation of Y_c , where T_{H_2} indicates the total volume of hydrogen produced.

$$Y_c = \frac{T_{H_2} \times M_{H_2} \times 3}{V_m \times W} \quad (3.4)$$

4 Results and Discussion

4.1 Rheological properties

The rheological properties of a paste to be used in screen printing are the key and need to be properly studied for successful and repeatable deposition of thin layers. The paste should present a suitable rheological performance, *i.e.*, a proper viscosity and a pseudoplastic/shear thinning behavior. If the paste has a high viscosity and stickiness difficulties in spreading the paste uniformly or clogging of the mesh are expected. On the other side, if the paste presents low viscosity and a liquid behavior, bleeding and poor adhesion to the substrate are common phenomena that may happen. For a high-quality coating, a balance between these different variables and their impact on paste rheology is essential, since it is directly related to quality of the catalytic layer. Therefore, nine pastes were formulated, and the dependency of the dynamic viscosity (Pa·s) on the shear rate (s^{-1}) was measured, as shown in Figure 10. The impact of increasing the Ni/SiO₂-Al₂O₃ content from 60 wt.% to 65 and 70 wt.% on propane-1,2-diol was also investigated. The same catalytic powder went through sequential milling processes, leading to smaller particles with increased surface area. The pastes prepared were hereafter called as T-SC, where T is the time in the ball milling and SC is the solid content in wt.%. It is important to mention that propane-1,2-diol is a Newtonian fluid presenting a viscosity value of approximately 0.053 Pa·s.

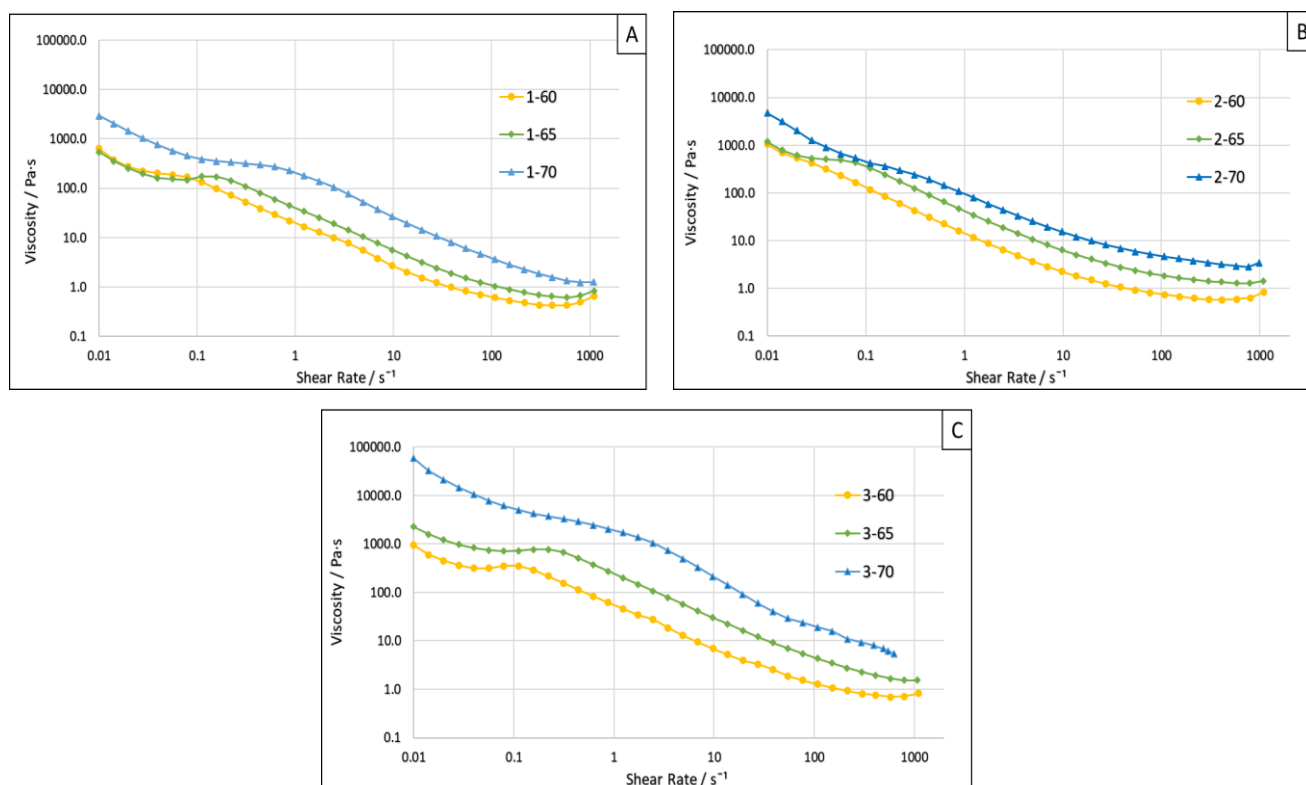


Figure 10 - Viscosity-shear rate curves for propane-1,2-diol pastes varying the time spent on the ball milling: 1 h (A); 2 h (B); 3 h (C).

All pastes presented a good shear thinning behavior, suggesting that the paste would easily flow during the squeegee action and application to the substrate. Besides that, increasing the solid content led to higher viscosity. This phenomenon probably occurs due to a higher network formation between the solid particle, entangling the liquid molecules and avoiding their movement. Additionally, a viscosity increase was observed for the samples that spent more time on the ball milling. When particles are milled multiple times, the particle size is progressively reduced, leading to a higher surface area to volume ratio. This may result in a larger contact area between the catalyst particles and the organic vehicle, which promotes a stronger interaction and enhanced network between them. Consequently, the viscosity of the sample tends to increase [67]. Appendix D compiles granulometric data about the studied powders. Just as the viscosity-shear rate curves, a small difference in particle size is observed between the first and second hours of the milling process. The 200 rpm rotational speed may not be sufficient to present a significant reduction on particle size. However, since the third milling step is more aggressive (400 rpm), a size reduction is observed in most of the samples, as well as a viscosity increase.

To select the pastes, the first criterion defined was the viscosity of the pastes at rest, *i.e.*, with a shear rate of 0.01 s^{-1} , which should be in the range of 500-1500 Pa·s. Pastes that presented a viscosity value higher than this limit were considered too thick, because it would make the coating process more difficult and with lower quality. Inversely, for lower viscosities, the risk of bleeding or seepage was considered high. Table 1 presents the paste viscosity at 0.01 s^{-1} for the nine pastes. All the pastes with 70 wt.% Ni/SiO₂-Al₂O₃ content were too viscous and inappropriate for screen printing, as well as the 3-65 paste.

Table 1 - Viscosity (Pa·s) values obtained at 0.01 s^{-1} for the studied pastes.

Sample	1-60	1-65	1-70	2-60	2-65	2-70	3-60	3-65	3-70
Viscosity (Pa·s)	637	543	2956	1050	1186	4756	940	2280	>5000

The second criterion selected was the structural recovery of the remaining pastes. The screen printing process can be divided in three steps: (1) before printing, where there is no applied shear rate and the ink is at rest; (2) during the squeegee action, responsible for pressing the paste through the mesh openings; (3) after the deposition on the substrate, where the paste is at rest again and must recover its properties. To replicate this scenario, a 3ITT method was carried out to analyze the dynamic changes in structure and viscosity, aiming to understand the thixotropic behavior by simulating the screen printing process [91]. On this time-dependent test, after an initial rest at low shear rate (0.1 s^{-1}), a strong shear rate (1000 s^{-1}) is applied for 0.6 s to replicate the structural breakdown during the squeegee action. After that, the regeneration is analyzed by stimulating rest at low shear again. According to Wang *et al.* [91], good structural recovery is achieved if at least 80 % of the initial viscosity is restored at the

end of the third interval. The recovery obtained and the required time to reach 80% of the initial viscosity after the stress are shown in Table 2. The obtained graphics are on Appendix E.

Table 2 - Recovery at the end of the 3ITT method and necessary time to achieve 80 % of the initial viscosity.

Sample	1-60	1-65	2-60	2-65	3-60
Recovery (%)	81.3	88.7	84.5	91.7	96.6
Time (s)	28	6	24	6	6

Based on the obtained results, it seems that the applied stress is insufficient to cause complete structural damage to the pastes network, since almost all the pastes demonstrated satisfactory performance. For all the pastes, the initial viscosity is high, which indicates that flowing and dripping would not occur. Then, a sharp decrease in viscosity is observed during the stress, meaning that the inner networks are rapidly damaged, which is also beneficial to the screen printing process. Finally, the paste gradually recovers its initial viscosity, preventing overflow and suggesting stability. Although all the pastes have potential for screen printing, the most promising are the ones with a higher recovery. Therefore, the three pastes with better recovery results, *i.e.*, 1-65, 2-65 and 3-60, were considered the best ones. Moreover, a tendency for better recovery on the pastes with smaller particles was observed.

The last selection criterion was the thixotropic index, which is the ratio of the viscosity measured at two different shear rates, generally different by a factor of 10 [91]. On this case, the selected values were 4 s^{-1} and 40 s^{-1} . In fact, this value measures the pseudoplasticity of the material, helping to determine the ability of the paste to maintain its shape on the mesh without dripping, while becoming fluid when the squeegee pressure is applied during the deposition process. Table 3 presents the thixotropic index of the better pastes.

Table 3 - Thixotropic Index of the selected pastes.

Sample	1-65	2-65	3-60
Thixotropic Index	6.87	4.68	6.55

The paste showing the highest thixotropic index presented a more significant drop in viscosity as the stress was increased. This indicates a better shear-thinning behavior, which is an optimal rheological property for screen printing. The combination of this characteristic with the high recovery presented previously may lead to a high-precision printing with sharper edges and increased stability. Therefore, 1-65 and 3-60 pastes are the ones that presented the best performance, being considered the best options for screen printing.

α -Terpineol was also tested as organic vehicle. As well as propane-1,2-diol, it presents suitable properties for screen printing. However, due to the molecular structure, propane-1,2-diol is a more polar compound. α -Terpineol has a larger and relatively more

complex cyclic structure, with only one alcohol functional group attached to it, which results in a low dielectric constant of 2.8 at 20 °C [92]. On the other side, propane-1,2-diol presents two hydroxyl groups attached to a small and linear propane chain, resulting in a more polar compound with a higher dielectric constant of 32.0 at 20 °C [92]. The interaction with the studied catalyst is intensified with propane-1,2-diol, since both Ni, at an oxidized stage, and alumina present polar behavior. This effect can enhance the dissolution ability by strengthening intermolecular interactions between the solvent and the catalyst. Moreover, the pastes composed by α -terpineol presented a huge stability issue. α -Terpineol has a melting point close to ambient temperature (18 °C), which leads to operation difficulties and undesirable phenomena, such as freezing. On the other side, propane-1,2-diol does not present such problem, since the melting point is -59 °C, which makes it a better organic vehicle at room conditions. Besides that, particles in the nanometer range are usually studied, presenting a most stable balance between the methane decomposition and carbon diffusion rate [39, 60]. Therefore, 1-60 (1 h of ball milling and Ni/SiO₂-Al₂O₃ content of 60 wt.% with an average diameter of 90 nm, in terms of number, obtained from the granulometric data) paste was selected for future tests.

4.2 Characterization of printed layers

After choosing the most suited screen printing paste, it was deposited through screen printing technique on the glass substrates to obtain the desired catalytic layer. The deposition was done on an area of *ca.* 1.77 cm². The snap-off distance, *i.e.*, the gap between the screen mesh and the substrate, responsible for defining the wet film thickness, was selected as the parameter under study. This criterion plays a crucial role in achieving a high-quality coating and controlling the amount of paste deposited across the substrate. The catalytic loading has a significant effect on the reaction performance, having a profound impact on the kinetics and stability of the catalyst. Therefore, five different snap-off distances were tested (0.8, 1.0, 1.2, 1.5, and 1.8 mm) and their impact on the substrate loading was analyzed. Table 4 shows the behavior of the screen printing (SP) coatings.

Table 4 - Information about the screen printing coatings.

Sample	SP-0.8	SP-1.0	SP-1.2	SP-1.5	SP-1.8
Snap-off distance (mm)	0.8	1.0	1.2	1.5	1.8
Catalyst deposited (mg)	2.77	2.88	3.09	3.34	3.74
Nickel deposited (mg)	1.80	1.87	2.01	2.17	2.43
Loading (mg _{cat} ·cm ⁻²)	1.57	1.63	1.75	1.89	2.12

Screen printed substrates showed a catalytic loading ranging from 1.50 to 2.20 mg_{cat}·cm⁻². As the snap-off distance increased, simultaneous growth in loading was observed. It is worth

noting that a snap-off distance of 2 mm was also tested, resulting in a completely blurred film with poorly defined borders. Considering a uniform particle distribution with diameters between 1 and 5 μm (particle size range that presents the most significant volume percentage according to the granulometric data), and a particle packing factor of 0.6, the formation of a monolayer would correspond to loadings between 0.41 and 2.05 $\text{mg}_{\text{cat}}\cdot\text{cm}^{-2}$, respectively. This indicates that the produced films are in the range for the formation of a monolayer. Figure 11 presents the variation overview of the substrate loading with the snap-off distance. At the tested interval, an approximately linear relationship was observed.

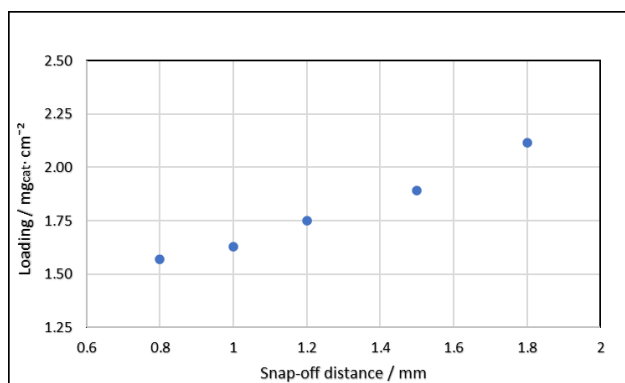


Figure 11 - Variation of the substrate loading with the snap-off distance for the prepared SP films.

The catalyst microstructure is one of the most important characteristics in the field of catalysis. The internal arrangement and morphology of the catalyst at a microscopic level play a crucial role in determining its activity and performance [66]. By controlling the intricate network of particles within the catalyst, it becomes possible to optimize its stability and enhance its overall performance. Therefore, to investigate the impact of the snap-off distance on the structure of the thin $\text{Ni}/\text{SiO}_2\text{-Al}_2\text{O}_3$ film, SEM images of the screen printed films were captured. Figure 12 presents the top-view images obtained, as well as its EDS chemical/elemental analysis, for the SP-0.8 sample, as an example. In general, all the prepared catalytic substrates presented a similar pre-reaction microstructure arrangement. Appendix F exhibits the obtained data for the remaining substrate. In Figure 12.A it is possible to observe the presence of several defects and cracks. This phenomenon can be caused by a rapid and inadequate drying method, which induces a high internal stress within the film while the solvent evaporates [93]. If the drying is too fast, the particles may not have time to arrange themselves in the desired structure [94]. Therefore, besides causing a reduced film quality, these imperfections can also be prejudicial for CMD reaction; the generated carbon can grow on those spaces, possibly leading to detachment of the catalytic film and limiting the surface area available for the reaction by pore clogging. However, it was observed that the film tends to spread out, possibly due to a stable bond between the catalyst and the substrate. No islands, clumps or empty spaces were observed in the center of the film, but edges are not well-defined, as shown in Figure 12.B. This can be caused by the squeegee action during the screen printing

procedure due to an unsuitable mesh quality or even solvent flow by capillary action during drying step. Figure 12.C shows that the particle size is heterogeneous. This uneven population prevents the formation of a monolayer. Additionally, a balanced element distribution was obtained (for SP-0.8: 29.26 wt.% of O; 54.88 wt.% of Ni; 8.32 wt.% of Si; 6.00 wt.% of C and 1.55 wt.% of Al), as well as minor C contamination - Figure 12.D. This indicates that the catalyst is uniformly dispersed throughout the substrate, without any significant concentration variation or segregation.

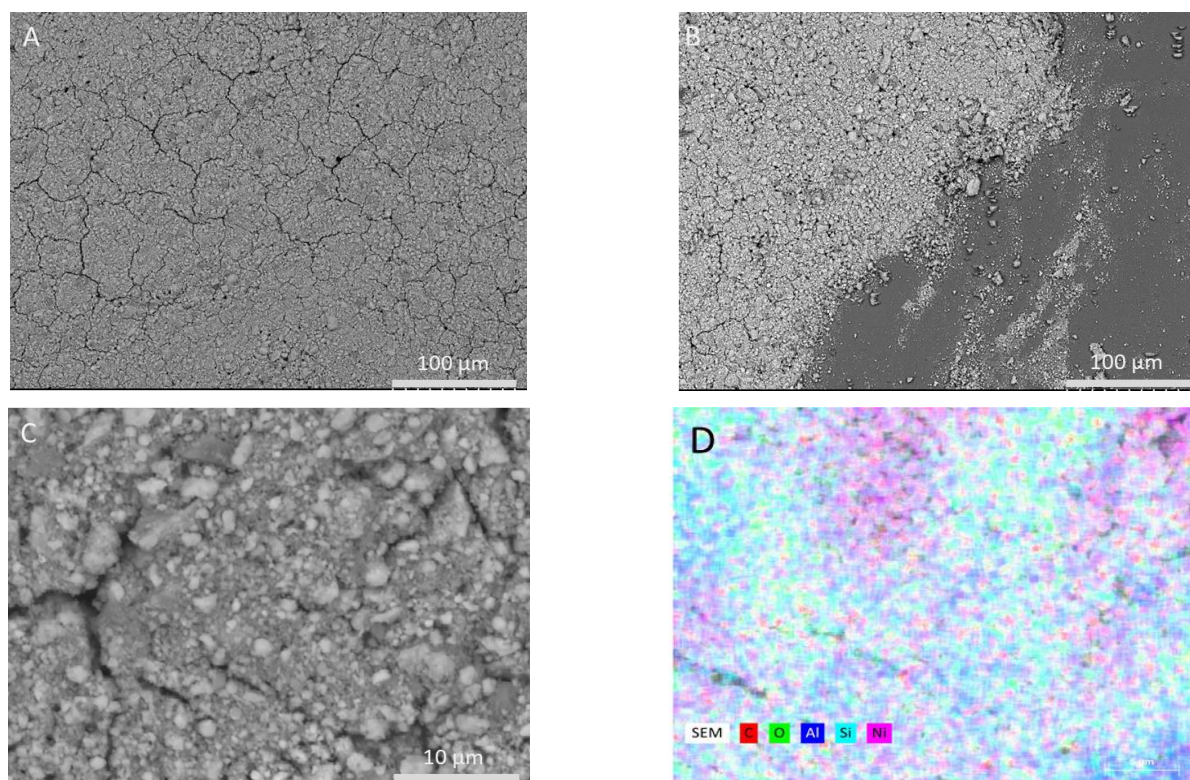


Figure 12 - Top-view SEM images (BSE mode, 15 kV) of the SP-0.8 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure 12.C (D).

Cross section SEM images FOR SP-0.8 sample shown in Figure 13 provided a perspective of the layer arrangement, allowing the examination of the film thickness, uniformity and presence of defects. The catalytic activity is a thickness-dependent parameter, being affected by the accessibility of reactant molecules to the catalytic sites. A thinner film presents a higher surface area per unit of volume, providing more available active sites for catalytic reactions. Besides that, a reduction in mass transport limitations is also observed in thin films when compared to thicker films. A thicker film, on the other side, may present a significant inactive portion that is not exposed to the reaction, decreasing the catalyst efficiency and provoking an underutilization of the material [22]. However, an undesirable phenomenon was observed on the screen printed samples, *i.e.* the film deposited was not uniform, suggesting that a catalytic monolayer is not formed. This phenomenon indicated that deposition of particles on top of each other occurred, as well as height irregularities, such as valleys. Appendix F exhibits the obtained cross-section images for the remaining substrates.

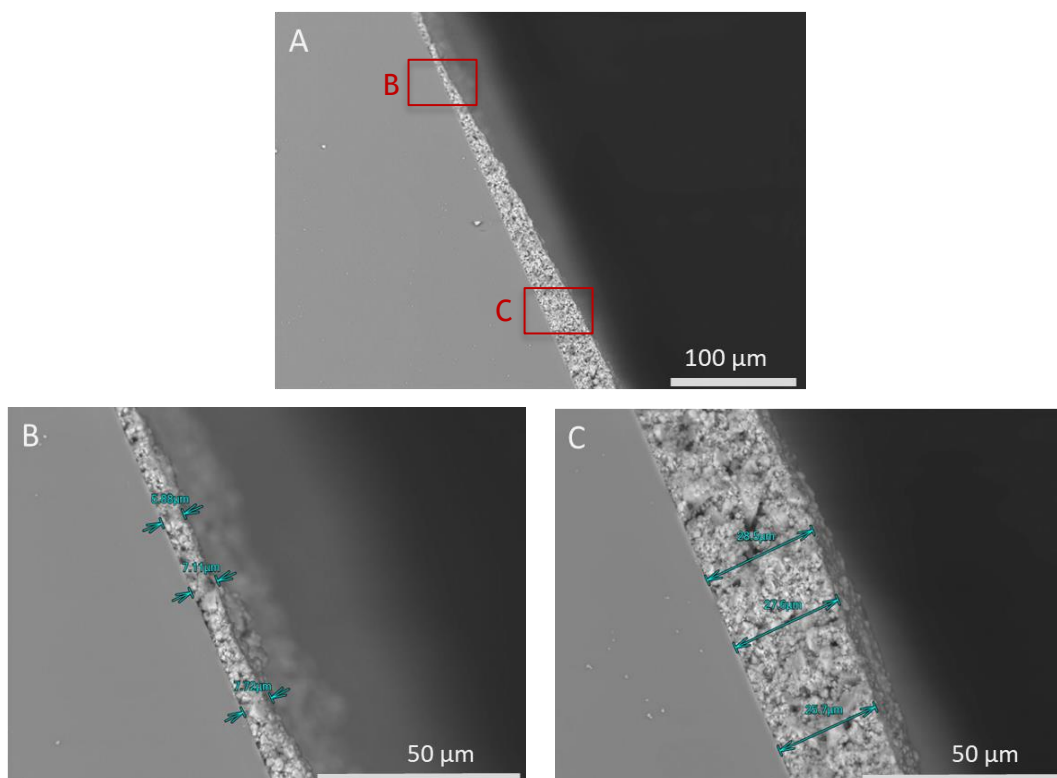


Figure 13 - Cross-sectional SEM images of the SP-0.8 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).

This occurrence was presented in all screen printed substrates. The origin of this phenomenon may be related to an uneven squeegee pressure distribution during the screen printing process or to an unsuitable drying technique. According to Garsany *et al* [94], a stationary drying promotes a non-uniform thickness due to different evaporation rates between the center of the sample and the edge. They observed that the evaporation flux is much higher at the edge than at the center, leading to more solvent loss at the edge. To compensate this behavior, capillary force may induce flow of the paste from the center to the edges, resulting in a non-uniform deposition by making the edges thicker than the center. Additionally, an inappropriate mesh quality may be a possible origin to this occurrence, generating thicker films on the mesh openings and thinner layers on the mesh wires. Despite that, an increase in the film thickness was observed while the snap-off distance was increased. However, to verify the real impact of the film thickness and microstructure on the catalyst behavior, CMD reactional tests should be performed. Table 5 presents the thickness variation of the thicker and thinner zones of the samples obtained through the cross-section measurements.

Table 5 - Thickness variation of the prepared screen printed substrates.

	Sample	SP-0.8	SP-1.0	SP-1.2	SP-1.5	SP-1.8
Thickness (μm)	Thinner zone	6.5	6.5	6.6	8.0	9.0
	Thicker zone	27.3	27.5	29.0	31.1	32.0

4.3 Catalytic Tests

The performance of the prepared catalytic substrates were evaluated through CMD reaction to study the effect of the snap-off distance and the catalyst loading on the catalyst activity, durability, and carbon yield. Unfortunately, due to low availability of the equipment and the time required for each test, it was not possible to evaluate all the prepared substrates. Figure 14 exhibits the H_2 activity obtained over 10 h for the tested substrates. It is important to highlight that the tests should be maintained until the complete deactivation of the catalyst to measure its lifetime.

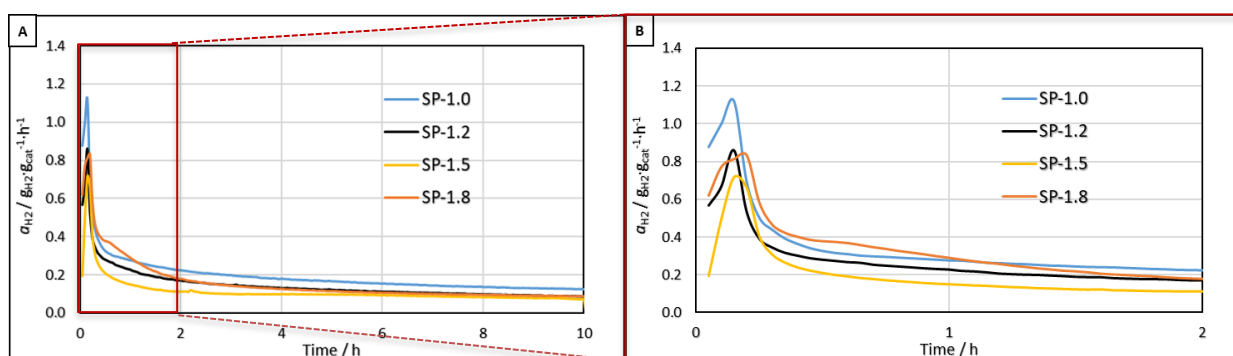


Figure 14 - H_2 activity over time for the substrates coated by screen printing: 10 h (A); zoom of first 2 h (B).

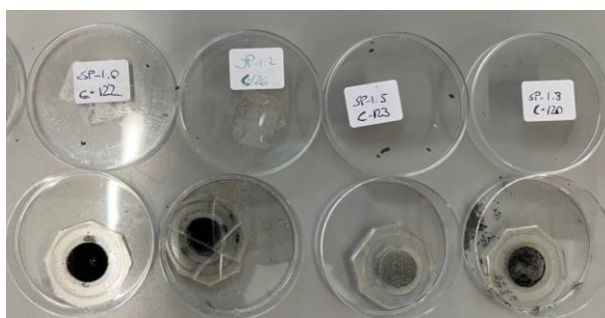
A similar catalytic activity behavior was observed for all samples, *i.e.* a high initial peak activity followed by a quick deactivation; more than half of the maximum activity was lost on the first 30 min of operation. This phenomenon may be related to the quality of the commercial catalyst used, which was not properly designed for reducing the carbon growth impact by the tip-growth mechanism and pore clogging, which, in turn, prevented the access of reactant to the active centers. Table 6 presents some important parameters obtained from the reactional tests, such as the average activity ($\bar{a}$), the maximum recorded activity (a_{max}) and Y_c for the tested period of 10 h. From Figure 14 and Table 6, SP-1.0 sample shows the highest activity, *i.e.* the best CMD reaction/h performance, which may be related to the approximation of a catalytic monolayer. The formation of a catalytic monolayer allows a higher surface area-to-volume ratio and, consequently, a more efficient utilization of the active centers. If particle overlap and agglomeration phenomena are avoided, a more stable and active layer is obtained. On the other side, as expected, increasing the loading allowed to reduce almost linearly the performance, except for SP-1.8 sample. This phenomenon suggested that some of the catalyst becomes inactive as the loading increases or there are diffusion limitations in the thicker films, which are consequently more distant from the ideal monolayer.

Table 6 - Reaction performance parameters obtained for the samples coated by screen printing.

Sample	Loading ($\text{mg}_{\text{cat}} \cdot \text{cm}^{-2}$)	a_{max} ($\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	$\bar{a}$ ($\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	Y_c ($\text{g}_c/\text{g}_{\text{cat}}$)
SP-1.0	1.63	1.12	0.20	5.85
SP-1.2	1.75	0.86	0.15	4.36
SP-1.5	1.89	0.72	0.12	3.36
SP-1.8	2.12	0.83	0.16	4.67

4.4 Post-mortem characterization

From the post-reaction film characterization by SEM, insights into the film stability, carbon growth mechanism and deactivation can be extrapolated. Figure 15 exhibits the samples after the reaction.

**Figure 15** - Substrates coated by screen printing after the reaction and their respective identification at the top.

Visually, it is evident that the samples with higher loading and thicker film presented a more severe detachment. From a snap-off distance of 1.5 mm, it was noticeable that the film adhesion to the substrate becomes weaker. This phenomenon indicates that these samples have less structural stability, which makes them unsuitable to be used CMD reactors. SP-1.8 presents a completely detached layer, which justifies the obtained activity profile (Figure 14), *i.e.* a slower deactivation due to reagent access to previously blocked active centers, resulting in a higher average activity. On the other hand, the thinnest film - SP-1.0, apparently maintained initial aspect, which possibly justifies the continuous deactivation profile, without increases in activity. Figure 16 presents some of the obtained SEM images for SP-1.0 and SP-1.2 films. SP-1.5 and SP-1.8 presented a similar level of detachment and failures - see Appendix G.

Through SEM images it was possible to detect some defects not observable with the naked eye and differences on the films before (Figure 12) and after the CMD reaction (Figure 16). Figure 16.A reveals surface defects and detachment of the film, possibly due to carbon growth, which in some cases can lead to irreversible damage on the microstructure. However, the film failures observed before the reaction (Figure 12.A and C) are less significant on *post-mortem* samples. The accumulation of the generated carbon may be responsible for the cracks cover, leading to a porosity reduction and, consequently, the formation of a compact layer. For SP-1.2,

some failures are also present, as can be observed on Figure 16.C. However, when comparing Figure 16.B and D, a notable difference was detected: the sample with a higher loading (SP-1.2) presents an uncompact layer. This indicates a low structural stability, *i.e.*, the film tends to detach and crumble due to carbon accumulation and lack of adhesion. SP-1.5 and SP-1.8 present films with a similar behavior, making them unsuitable for this operation when compared SP-1.0. Moreover, the EDS analysis indicated a significant carbon concentration, mainly in the cracked areas (Appendix G). However, due to the low overall carbon production and microscope resolution, no images of the generated carbon were captured.

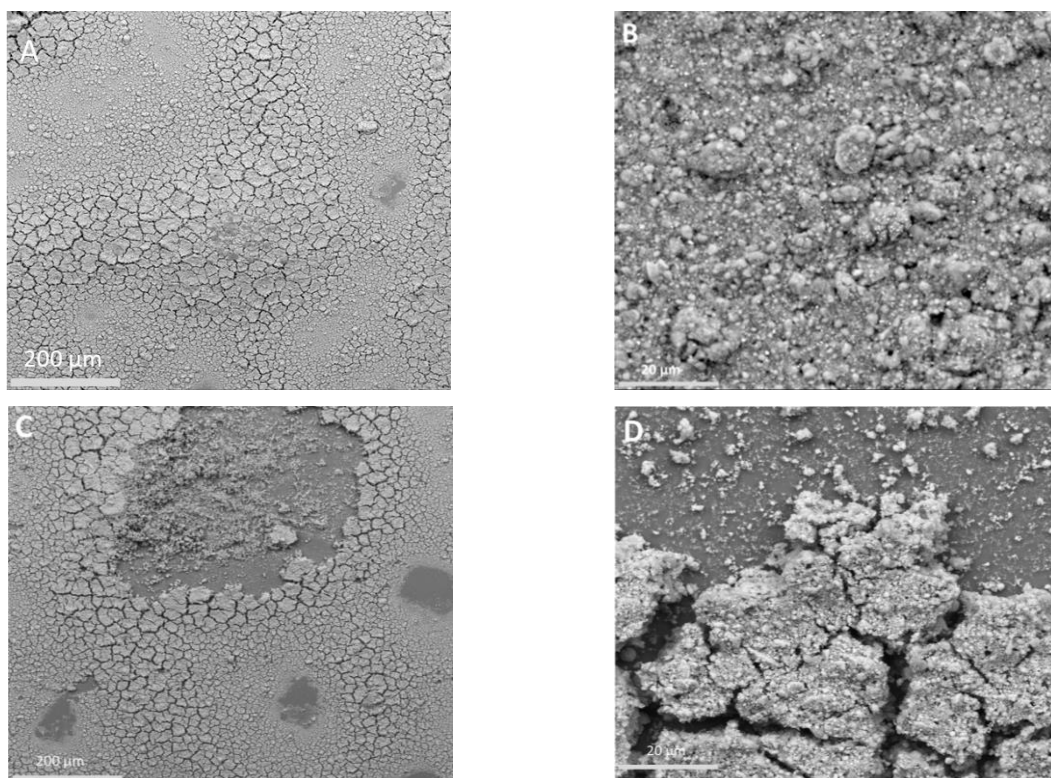


Figure 16 - Top-view SEM images of post-mortem samples: SP-1.0 - x300 (A) and x3000 (B); and SP-1.2 - x300 (C) and x3000 (D).

To solve the film detachment and lack of adhesion problems, several alternatives are possible. The addition of a binder on the paste formulation must be considered since it may increase the film interaction with the substrate, leading to a stronger adhesion [67]. Besides that, the employment of surface pre-treatments before the deposition may enhance the coating adhesion [95]. Concerning the reaction process, the catalyst lifetime can be increased promoting cyclic regeneration steps, as previously patented by UPORTO/Pixel Voltaic teams [16]. If the originally available openings and pores are not completely blocked by carbon, regeneration processes can be a solution to partially restore the catalytic activity of the film.

4.5 Regeneration Test

Despite being a promising technology to produce CO_x-free hydrogen, the catalyst fast deactivation represents a major drawback for the implementation of CMD. Carbon

accumulation and morphology changes of the catalyst during the reaction are some of the main responsible for stopping the process. The adoption of regeneration cycles can be a possible solution to restore the catalyst activity and obtain continuous operation. Through regeneration, the carbon deposits can be removed, partially restoring the catalyst initial structure. The regeneration was performed according to Pixel Voltaic/UPORTO patent [16]. Differently of other regeneration processes, such as combustion and steam gasification, the carbon hydrogenation would not generate GHG. During the regeneration test, a good contact between the gas phase and the carbon-catalyst interface is essential. Therefore, the decomposition step was performed for 60 min to ensure that the pores presented in the catalytic film are not completely covered by the generated carbon. Since SP-1.0 presented the best CMD performance, it was selected to conduct the hydrogen gasification for regeneration. Figure 17 presents the comparison between the unregenerated SP-1.0 process and the regenerated one.

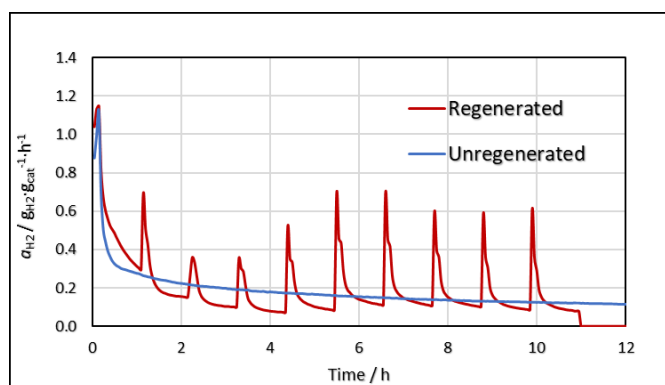


Figure 17 - Comparison of the H_2 activity over time between cyclic regeneration with hydrogen and unregenerated systems using SP-1.0 sample. For the regenerated catalyst, only the decomposition steps of each cycle are displayed.

Through Figure 17 it is possible to observe that the hydrogen regeneration can partially recover the catalyst activity. After the first cycle, a permanent deactivation occurred, which may be related to the carbon growth, *i.e.* the CMD reaction is very aggressive to the catalyst, possibly generating irreversible damage to the film mainly by the tip-growth mechanism. Besides that, between cycles 2 and 4, a stronger deactivation is observed. However, the following cycles show a higher activity peak. This phenomenon may be caused by the random growth of carbon during decomposition. In general, an almost constant activity recovery is noted, indicating a film with high stability is obtained. The quick deactivation presented on the beginning of each decomposition may be associated with the overall performance of the utilized commercial catalyst.

The regeneration process was performed for 5 min using a flow rate of $5 \text{ mL} \cdot \text{min}^{-1}$. Since the reactor presents a high volume comparatively to the film, an excess of hydrogen is used to ensure a sufficient hydrogen concentration for the reverse equilibrium reaction to occur. Since the utilized gas chromatography equipment only acquires data every 3 minutes, it is not possible to completely follow the regeneration process. However, well-established shock waves were

observed during cyclic decomposition and regeneration operations, as shown in Appendix H. Besides that, due to the lack of resolution of the equipment, a unique X_{H_2} point was able to be calculated, indicating a conversion of 20.6 %. Because of this, an arithmetic average over this cycle was considered, resulting in an approximate conversion of 10%. Assuming this regeneration conversion for the entire process, a total of 79 mL of hydrogen were produced (NPT conditions), corresponding to $ca. 2.05 \text{ g}_{H_2} \cdot \text{g}_{cat}^{-1}$ ($6.16 \text{ g}_C \cdot \text{g}_{cat}^{-1}$). Besides that, an average activity of $ca. 0.22 \text{ g}_{H_2} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$ was observed for the regenerated sample, which is higher than the unregenerated values presented on Table 6. This indicates that despite using a non-optimal commercial catalyst, the regeneration prevents its quick deactivation on the beginning of each decomposition. The operation time was sufficient to demonstrate better results with regeneration, but longer periods would provide a clearer understanding of its influence, since they would probably reveal the irreversible deactivation of the catalyst without regeneration, emphasizing the importance of the regeneration process.

4.6 Comparison with wet spray

A comparative study was conducted to assess the coating quality and performance of screen printing and wet spray techniques; the latter technique was optimized by Pixel Voltaic/LEPABE groups for this application. This study aimed to evaluate the characteristics, effectiveness, advantages, and limitations of both methods in achieving desired coating outcomes.

To enable a comparison between the two techniques, coatings with similar loadings were prepared on the same substrate (glass). An area of $ca. 3.14 \text{ cm}^2$ was coated. The substrates characteristics, such as the volume of the $5 \text{ mg} \cdot \text{mL}^{-1}$ solution utilized and loadings are presented on Table 7. It is important to point out that, in this study, higher loadings were obtained compared to those usually obtained by the research group. This could be attributed to the use of smaller catalyst particles, which may have promoted higher levels of deposition.

Table 7 - Information about the wet spray coatings.

Sample	Sprayed volume of the $5 \text{ mg} \cdot \text{mL}^{-1}$ solution (mL)	Catalyst deposited (mg)	Nickel deposited (mg)	Loading ($\text{mg}_{cat} \cdot \text{cm}^{-2}$)	Losses (%)
Spray-2.5	5	7.91	5.14	2.52	68.4
Spray-7.5	15	23.48	15.26	7.47	68.7
Spray-9.2	15	28.93	18.80	9.21	61.4

Table 7 clearly demonstrates the significant difference in catalyst quantity required for both techniques. While a minimum amount of 5 g of catalyst was necessary for screen printing due to utilization of the ball milling equipment, the wet spray technique only required 100 mg of catalyst (equivalent to 2 % of the screen printing amount) to produce 20 mL of the sprayed solution. Furthermore, it was observed that increasing the volume of the sprayed solution

resulted in a significant loading increasing, where the different loadings presented by sample SP-7.5 and SP-9.2 was a direct result of the spray gun position. However, the adhesion of new particles over the deposited ones and cohesive force between them can be a problem, leading to surface defects and even detachment [96]. A substantial amount of catalyst was found on the protective mask, contributing to these losses; this may happen due to an incorrect spray gun positioning or particle bounce after reaching the surface. Additionally, a small amount remained on the solution container and on the spray gun, mainly due to sedimentation effects. However, losses are higher in percentage for small areas, but they can become much lower when the process is upscaled.

The impact of different catalyst loadings on the microstructure and morphology of the thin layer was studied by SEM. Figure 18 shows the images obtained for samples Spray-2.5 and Spray-7.5, since Spray-7.5 and Spray 9.2 were expected to have similar microstructure. Appendix I compiles the additional images and the EDS analyses. In Figure 18.A and C is possible to observe that sample Spray-7.5 has a thicker and denser layer than Spray-2.5 (an average of 45.3 μm and 17.2 μm , respectively). This phenomenon is related to the larger amount of catalyst deposited during the wet spray process. Contrarily to the screen printed samples, no significant variation of thickness across the substrates was observed. However, the presence of a thicker and denser layer may prevent the access of methane to the bulk catalyst due to diffusion limitations and mass transport resistances. Furthermore, a thicker layer causes a higher covered portion of the catalytic layer, leading to a significant inactive portion, which decreases the catalyst efficiency and provokes an underutilization of the material. In addition to that, Figure 18.B and D show that the generated film is not uniform, presenting several irregularities that was not observed on the SEM cross-section images. This condition may be caused by the particle over particle adhesion, since it may not be as efficient as particle over substrate adhesion in terms of achieving a uniform and tightly packed coating. Due to this lack of adhesion, the recently sprayed particles collide with the stable ones and are possibly expelled. On the other hand, a favorable condition for particle attachment on the particle over substrate adhesion may occur as result of the more stable and structured surface, leading to an improved film quality. The substrate, different from the deposited particles, may act as a more stable solid foundation, allowing better uniformity. It is important to mention that images of the coating boundaries were not captured because they were poorly defined with naked eye. As with the screen printed samples, the EDS analysis (Appendix I) indicated a uniform distribution of the components along the substrate.

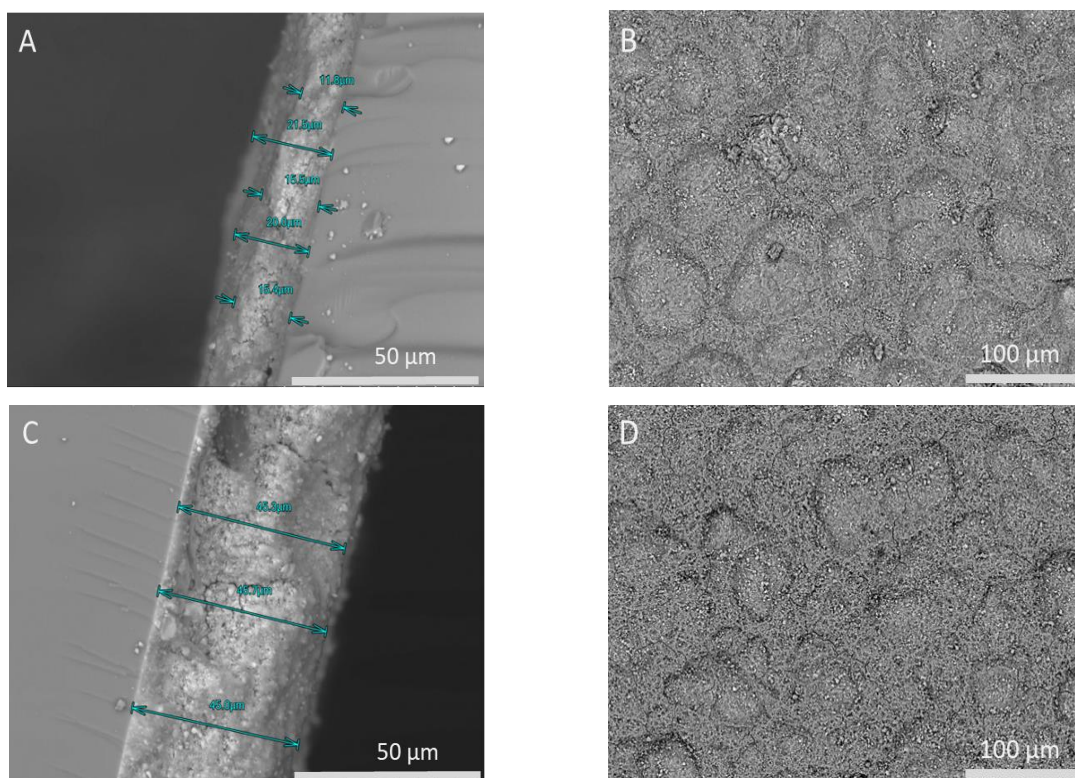


Figure 18 - SEM images of the wet spray samples: cross section - x1000 (A) and top-view - x300 (B) for Spray-2.5; cross section - x1000 (C) and top-view - x300 (D) for Spray-7.5.

To effectively compare the deposition methods, CMD reactional tests were performed on the substrates coated by wet spray. Spray-2.5 presented a loading similar to SP-1.8 that consequently makes them suitable candidates for a comparative study between the two deposition methods. Figure 19 shows the H_2 activity evolution over time for these samples.

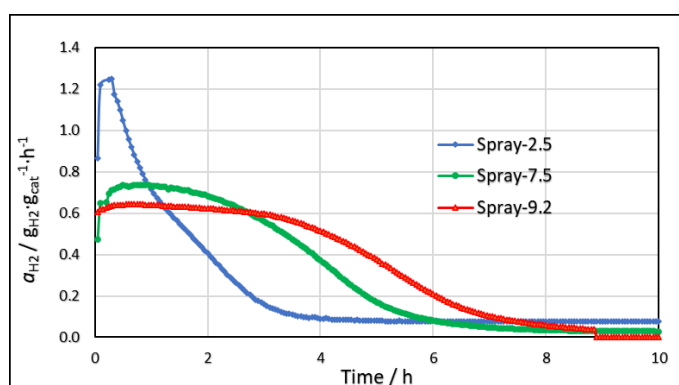


Figure 19 - H_2 activity over time for the catalytic substrates coated by wet spray method.

For samples Spray-7.5 and Spray-9.2, it can be observed from Figure 18.C that the higher amount of catalyst deposited (20-30 mg) resulted in thicker and denser layer. However, this may have led to diffusion limitations and underutilization of the catalyst, resulting in a significant inactive portion and lower activity levels. Interestingly, unlike the others samples, these two showed an almost constant activity for 3 h without significant loss, followed by gradual deactivation. Regarding Spray-2.5, with 3 times less catalyst than the other spray samples and a thinner film, a behavior more similar to the screen printing samples was

observed. It exhibited a high initial activity peak followed by a faster deactivation rate. Table 8 presents a useful overview of the data collected for the 10 h operation of the spray samples.

Table 8 - Reaction performance parameters of the samples coated by wet spray.

Sample	Loading ($\text{mg}_{\text{cat}} \cdot \text{cm}^{-2}$)	a_{max} ($\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	$\bar{a}$ ($\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	Y_c (gC/g_{cat})
Spray-2.5	2.52	1.25	0.23	7.13
Spray-7.5	7.47	0.74	0.30	9.11
Spray-9.2	9.21	0.64	0.39	10.27

The deactivation rate can be evaluated by comparing $\bar{a}$ with a_{max} . Spray-7.5 and Spray-9.2 clearly have a slower deactivation than Spray-2.5 that presented a worst performance and efficiency. However, a comparison of the samples coated by wet spray after reaction, displayed on Figure 20, suggests that a severe detachment occurred on these samples.

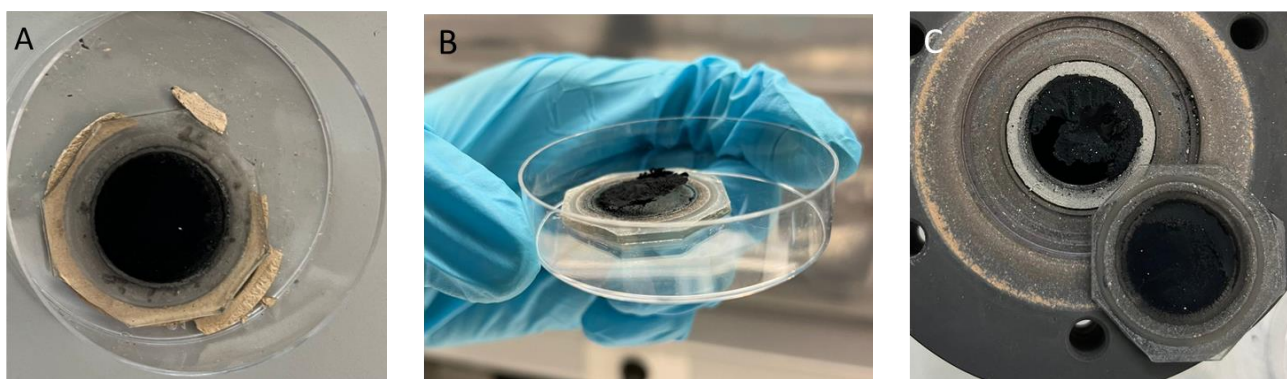


Figure 20 - Naked eye post-mortem images of: Spray-2.5 (A); Spray-7.5 (B); Spray-9.2 (C).

When observed by naked eye, sample Spray-2.5 kept its initial structure, but Spray-7.5 and Spray-9.2 presented a complete fragmentation of the catalytic film. Therefore, the higher production level presented by these samples can be related to a layer destruction due to the carbon generation, which possibly opens access for methane to interact with non-deactivated layers. The inappropriate particle over particle adhesion may be responsible for the lower structural stability. Compared to the other substrates, the catalytic film of Spray-2.5 was not destroyed, suggesting that the highest activity drop may be caused by pore clogging. Still, since it maintains its initial structure, it becomes more interesting for the possible adoption of regeneration processes. Moreover, the H_2 activity profiles indicate that Spray-2.5 catalytic layer is closer to a monolayer. Figure 21 presents the *post-mortem* SEM characterization of this sample. For Spray-7.5 and Spray-9.2, since an almost complete detachment of the catalytic layer occurred, SEM analysis was not conclusive. As can be observed on Figure 21.A, the defects presented on Figure 18.B were not present. The carbon accumulation during the reaction may be responsible for covering the defects, leading to the formation of a compact layer. Besides that, it was possible to detect the generated carbon since the production was higher than the

obtained for the samples coated by screen printing. Figure 21.B reveals the presence of carbon filamentous, along with Ni particles on the top of these filaments, suggesting the occurrence of a tip-growth mechanism.

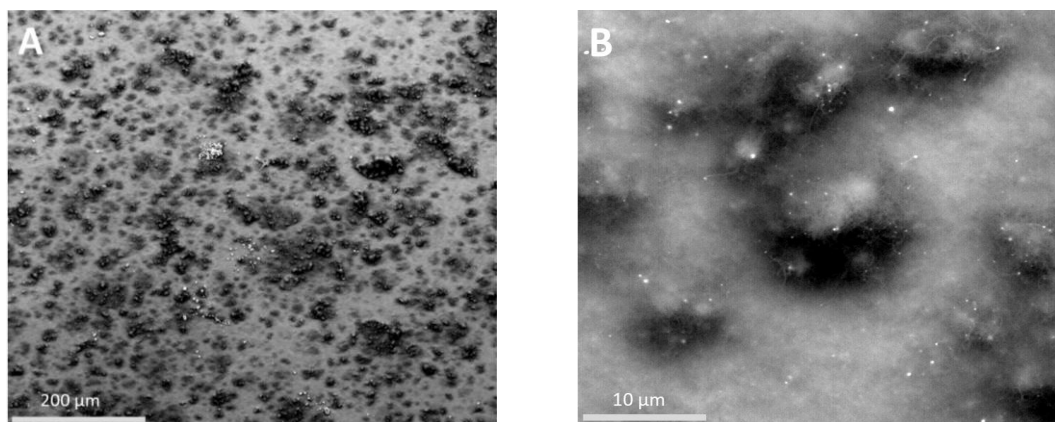


Figure 21 - Post-mortem SEM images of Spray-2.5 sample: top view of the center of - x300 (A); top view approximation of the center of Spray-2.5 - x6700 (B).

The catalytic activity over time comparison between SP-1.0, SP-1.8 and Spray-2.5 samples is presented on Figure 22. SP-1.8 and Spray-2.5 have a similar catalyst loading of $ca. 2.5 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ on the same substrate, with the only difference being the coating method used. Table 6 and Table 8 display that the sample coated by screen printing had an overall worst performance, presenting a lower initial activity and lower values of normalized production ($\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1}$). Additionally, the $\bar{\alpha}$ values indicated a higher activity loss rate, which may be related to the poor adhesion of the film as well as the high presence of cracks, phenomena that lead to the detachment of the catalyst and its consequent deactivation due to carbon growth. The tested samples (Figures 15 and 20.A) also indicated that the thin film coated by wet spray presented a higher structural stability. Spray-2.5 maintained its initial structure, while a significant detachment was observed on SP-1.8. Therefore, based on the studied loading, it can be concluded that the wet spray method is preferable for producing a more stable and with higher activity $\text{Ni}/\text{SiO}_2\text{-Al}_2\text{O}_3$ film. When comparing Spray-2.5 with SP-1.0, the best screen printed sample, a similar initial peak was observed. However, possibly due to a better structuring of the layer (no unevenness) and the larger catalyst mass, deactivation occurs more slowly on the spray sample.

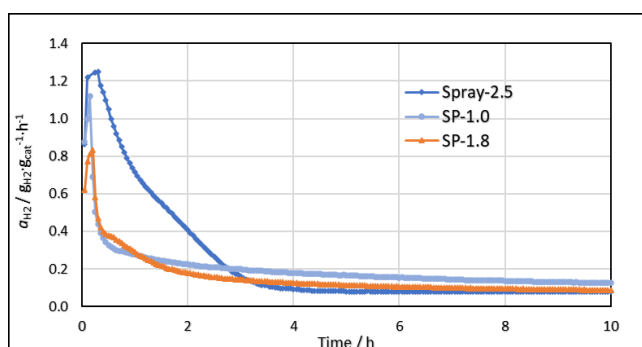


Figure 22 - H_2 activity over time comparison between: Spray-2.5, SP-1.0 and SP-1.8.

5 Conclusion

Methane decomposition emerges as a promising technology for clean hydrogen production. Low temperature reaction can be operated at *ca.* 500-650 °C, offering a less energy-intensive process compared to more mature high-temperature methods. Despite its potential, CMD suffers from carbon clogging issues. To address these challenges, the search for highly active and stable catalysts is essential and Ni-based materials are a suitable choice. Catalytic thin films have unique properties that can favor this reaction, such as high surface area to volume ratio and the use of small amounts of catalyst; however, they need to be deposited using a reproducible, scalable and cheap technique. In the present work, screen printing (SP) method was systematically optimized to deposit commercial Ni/SiO₂-Al₂O₃ catalytic films on glass substrates; it was compared with wet spray technique that is currently used at LEPABE.

A suitable paste for screen printing was selected through a rheological study, using propane-1,2-diol. Three different solid loadings (60, 65 and 70 wt%) were considered, and ball milling was employed to mix the materials and produce a homogeneous paste. Increasing the ball milling intensity and milling time, smaller particle sizes are formed, presented increased surface area to volume ratio, stronger interparticle forces, and higher paste viscosity. All the produced pastes exhibited suitable pseudoplastic behavior necessary screen printing deposition. Paste 3-60 (3 h of ball milling and Ni/SiO₂-Al₂O₃ content from 60 wt.%) was selected due to its suitable viscosity at rest (shear rate of 0.01 s⁻¹), excellent recovery performance on 3ITT, high thixotropic index (indicating a significant drop in viscosity when stress is applied) and lower particle size population.

During the SP deposition, the snap-off distance was the main parameter under study; an increase from 0.8 mm to 1.8 mm promoted a rise in the catalytic loading, ranging from 1.5-2.5 mg_{cat}·cm⁻². However, SEM images revealed that the resulting films were not uniform despite the film thickness increase with the distance. The film microstructure plays a crucial role in the catalytic performance, affecting active sites accessibility, stability, and transport phenomena. Cracks were also observed, which can generate detachment and, consequently, deactivation due to carbon accumulation. Both phenomena are possibly related to an unsuitable drying method - capillary forces can drastically affect the film morphology. Uneven force distribution by the squeegee during the SP process can also influence the non-uniformity.

Regarding the reactional results, all the substrates presented a similar behavior: a high initial activity followed by a very fast deactivation, which may be related to the commercial catalyst utilized, which is not properly designed for aggressive carbon growth during CMD. The highest $\bar{\alpha}$ and ratio of products per mass of catalyst were obtained for SP-1.0 (0.20 g_{H2}·g_{cat}⁻¹·h⁻¹ and 5.85 g_C·g_{cat}⁻¹). Disregarding SP-1.8, which presented a collapsed film, a better reactional

performance was observed for the substrates with lower loading. This phenomenon indicates that diffusion limitations for the higher loading/thicker films may have occurred. In addition, the thicker samples, starting from SP-1.2, showed a high level of detachment after the reaction, while the thinner film showed better adhesion. An additional regeneration test was performed on SP-1.0, where a cyclic regeneration process with a small fraction of the produced hydrogen was studied. A permanent loss of activity was observed in the first cycle, possibly due to pore plugging or irreversible damage to the film, such as catalyst particles that were lost due to tip-growth mechanism. However, on the subsequent cycles, a constant activity recovery was obtained, indicating an acceptable structural stability of this system. The efficiency of the regeneration method was also confirmed, since for the same operation time, the regenerated sample produced more than the unregenerated (2.05 and 1.95 $\text{g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}$ respectively), besides delaying the deactivation.

To conduct a comparative study, catalytic films were also deposited through wet spray; the obtained films exhibited a uniform thickness but with imperfections, possibly due to particle adhesion issues during the deposition process. Films with a higher loading presented a thicker catalytic layer. Reactional tests revealed that substrates with higher loadings ($>7.5 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$) presented an underutilization of the material. The higher thickness led to potential diffusion limitations, resulting in an inactive portion and lower initial activity. Despite that, they presented a lower deactivation rate, when compared to substrates with lower loadings. However, a layer detachment due to carbon accumulation was observed, which possibly enabled the contact of methane with non-deactivated layers. The low structural stability displayed by them was not observed on the wet spray substrates with a lower loading ($2.5 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$), making it more suitable for longer operations and potential regeneration studies. SP substrate prepared with similar loading (SP-1.8) presented a lower structural stability since a film detachment after the reaction was observed, probably due to lack of adhesion. The wet spray sample presented a higher initial activity, average activity and carbon yield; a similar initial peak activity was observed for SP-1.0. However, possibly due to a better layer structuring and larger catalyst mass, deactivation occurs more slowly on the spray sample.

The main conclusions to withdraw from this study were: 1) the paste rheology is extremely dependent on the particle size, being the ball milling intensity and duration crucial to produce a suitable paste; 2) for screen printing with 0.8 mm, the snap off distance raise produced thicker films with higher catalytic loading; 3) substrates with lower loadings showed a more structurally stable film, exhibiting greater adhesion, while higher loadings resulted in detachment and collapse of the layer; 4) thicker films resulted in a significant inactive catalytic zone due to particle overlap and diffusion limitations, moving away from the formation of a monolayer and, consequently, exhibiting lower activity levels; and 5) the utilization of a cyclic regeneration process can improve catalytic lifetime.

6 Assessment of the work done

6.1 Objectives achieved

This study has contributed valuable insights for the low-temperature catalytic methane decomposition field, namely for the catalytic substrates and film deposition techniques. Specifically, screen printing was used for the first time for the deposition of Ni-based catalytic films for methane decomposition. The study provided useful knowledge in the field of rheology and rheological evaluation methods, one such method is the 3ITT, which proved to be effective in simulating the action experienced during the screen printing process. This technique holds significant value for the characterization of pastes in general. According to the characterization methods used, it was possible to produce a catalytic film with *ca.* $1.63 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$ able to maintain its structure during the reaction and achieving an $\bar{\alpha}$ of *ca.* $0.20 \text{ g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. Furthermore, its functionality was verified by adopting a cyclic regeneration test, where part of the activity was constantly recovered, achieving a higher $\bar{\alpha}$ and Y_c ($0.22 \text{ g}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ and $6.16 \text{ g}_c \cdot \text{g}_{\text{cat}}^{-1}$, respectively). Therefore, it was possible to develop another method for the deposition of Ni-based catalytic films and compare it with currently applied methods used at LEPABE and Pixel Voltaic in the search for stable and efficient catalytic substrates.

6.2 Future work

Screen printing remains a promising technique due to its scalability potential, however, future research must be done to optimize its effectiveness. The utilization of alternative drying methods can be a solution to the non-uniform thickness and presence of imperfections. Besides that, surface preparation through chemical and/or physical treatments, as well as the addition of a binder to the paste composition, can enhance the film adhesion. The testing of other substrates should also be performed. The employment of additional characterization techniques, such as XRD, Raman spectroscopy and XPS are also interesting to gain a deeper understanding of the carbon growth mechanisms and film behavior during the reaction. XRD would provide valuable insight into the crystalline phases of the catalytic film, before and after reaction, helping to understand its influence on the activity and stability. The chemical bonds presented in reduced and spent Ni/SiO₂-Al₂O₃ catalytic layer could be characterized by XPS, allowing a better understanding of the carbon growth mechanism and the generated carbon structures. Raman may be used to analyze the generated carbon structure and the growth mechanism. The adoption of alternative catalysts, specially designed for the CMD reaction, such as catalysts that promote base-growth mechanism, should also be tested. Therefore, further work must be performed to adapt screen printing for the deposition of thin catalytic films for CMD and, consequently, implemented on a large-scale production.

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Annex A - Supplementary figures

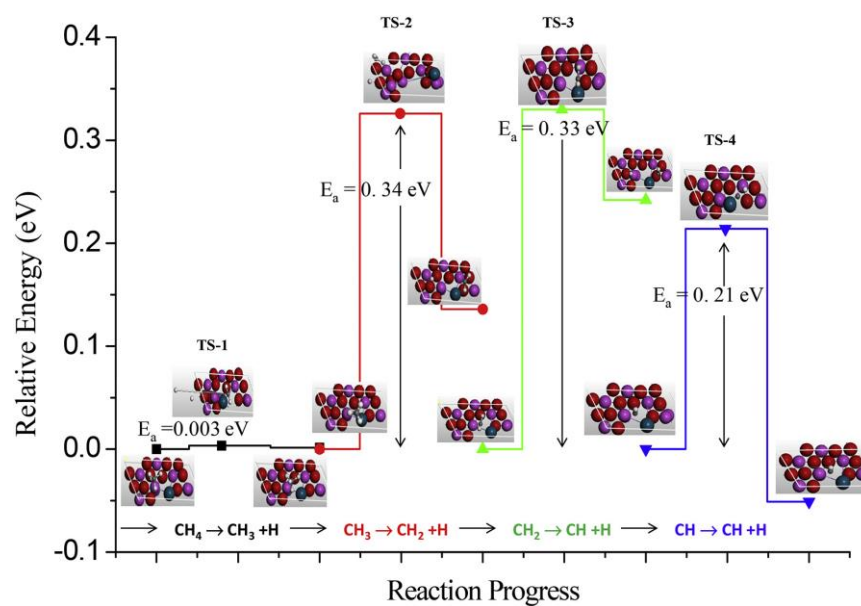


Figure A.1 - Density-functional theory study of progressive dehydrogenation of methane on Ni/Al₂O₃ (001) catalyst surface (extracted from [36]).

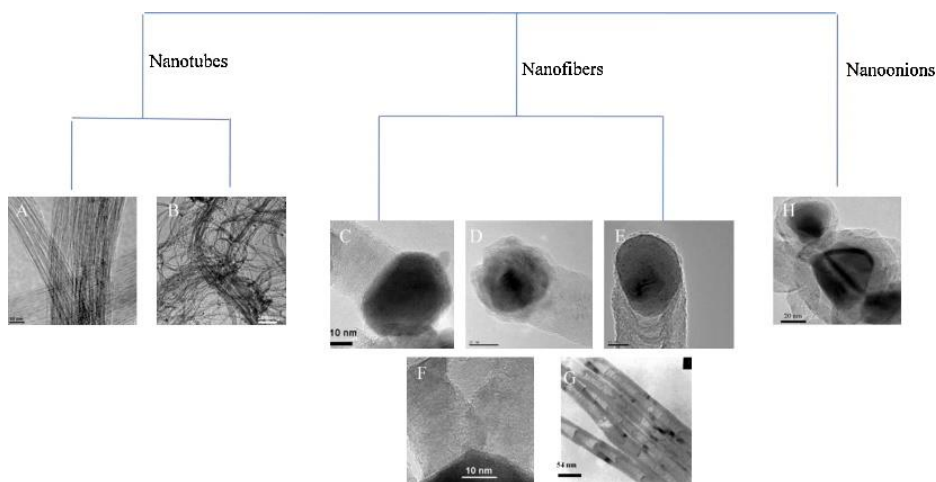


Figure A.2 - Compilation of some of the possible generated carbon structures (extracted from [35]).

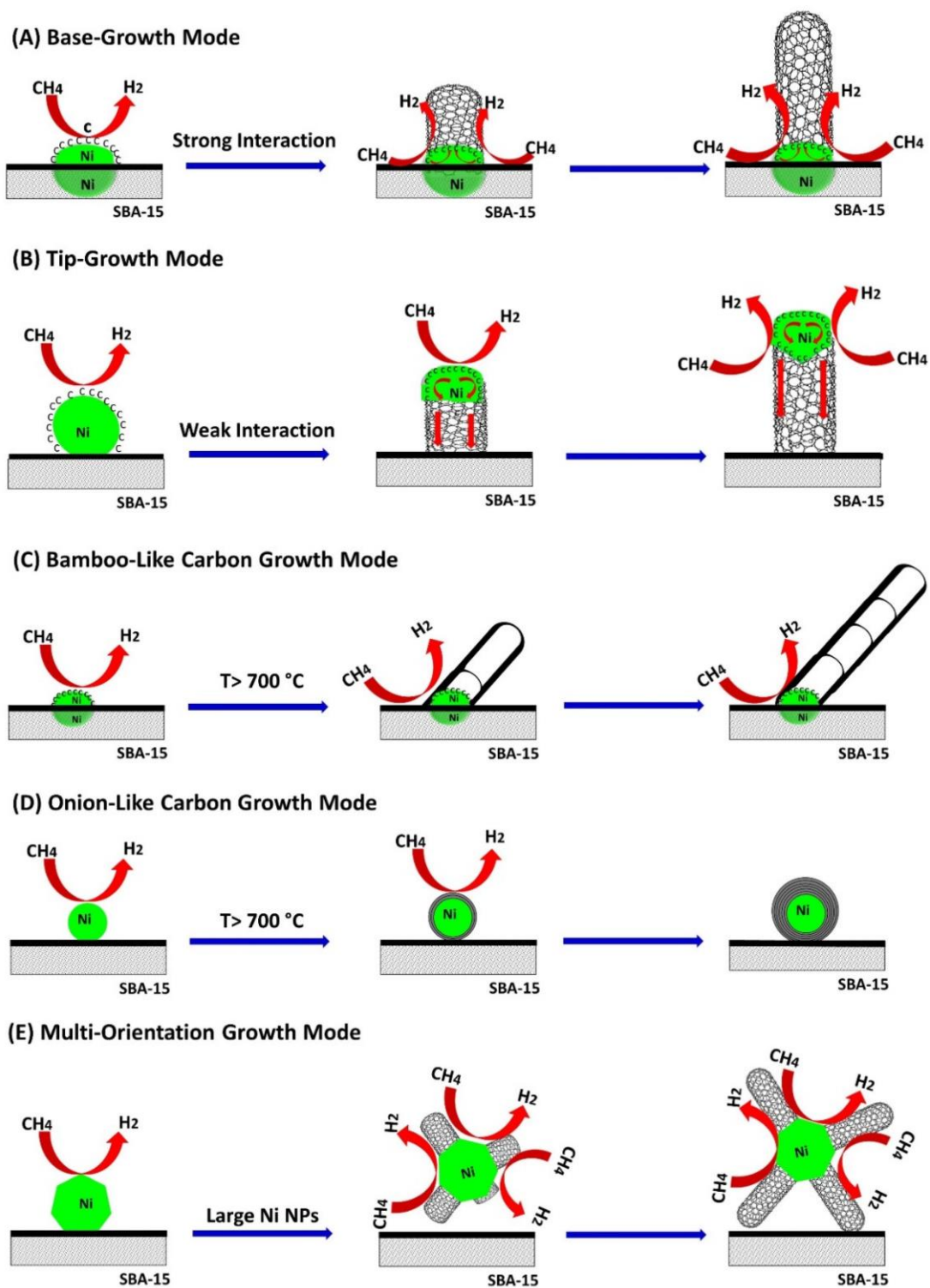


Figure A.3 - Examples of nanocarbon growth mechanisms on Ni/SBA-15 (extracted from [97])

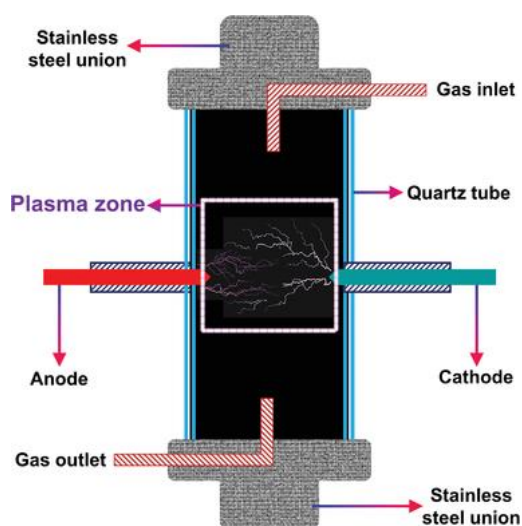


Figure A.4 - Schematic representation of the plasma reactor (extracted from [31]).

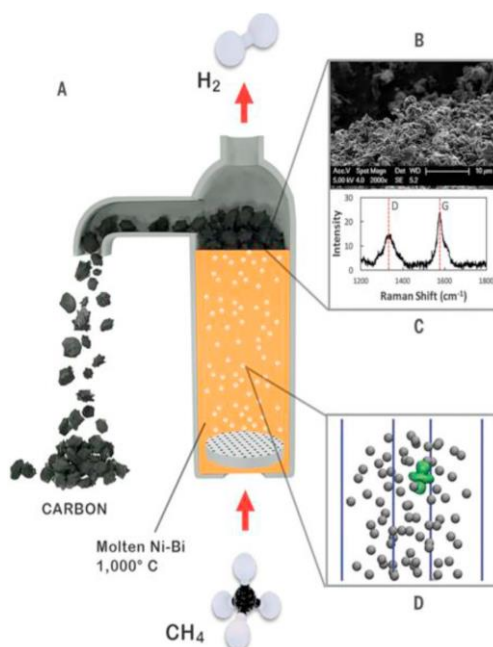


Figure A.5 - Schematic representation a molten metal reactor (extracted from [98]).

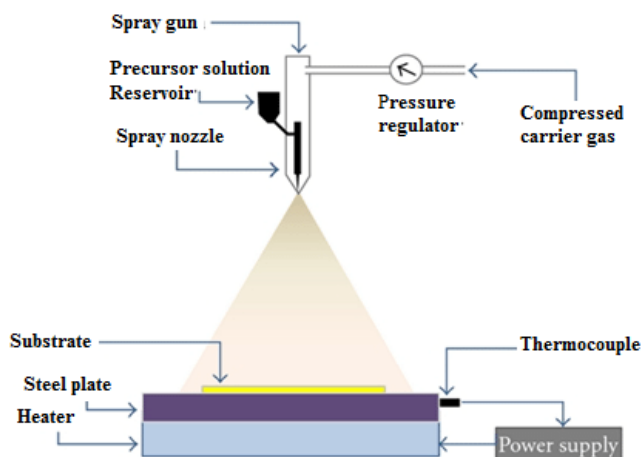


Figure A.6 - Schematic diagram of a wet spray setup (extracted from [66]).

Appendix A - Methane decomposition adsorption mechanism

Table A.1 - Sequential mechanism for methane dissociative adsorption and non-dissociative adsorption [26, 32, 33].

Step	Dissociative Adsorption	Non-Dissociative Adsorption
1	$CH_4 + 2S \rightleftharpoons CH_3 \cdot S + H \cdot S$	$CH_4 + S \rightleftharpoons CH_4 \cdot S$
2	$CH_3 \cdot S + S \rightleftharpoons CH_2 \cdot S + H \cdot S$	$CH_4 \cdot 2S \rightleftharpoons CH_3 \cdot S + H \cdot S$
3	$CH_2 \cdot S + S \rightleftharpoons CH_1 \cdot S + H \cdot S$	$CH_3 \cdot S + S \rightleftharpoons CH_2 \cdot S + H \cdot S$
4	$CH \cdot S + S \rightleftharpoons C \cdot S + H \cdot S$	$CH_2 \cdot S + S \rightleftharpoons CH_1 \cdot S + H \cdot S$
5	$C \cdot S \rightleftharpoons C + S$	$CH \cdot S + S \rightleftharpoons C \cdot S + H \cdot S$
6	$2 H \cdot S \rightleftharpoons H_2 + 2S$	$C \cdot S \rightleftharpoons C + S$
7	-----	$2 H \cdot S \rightleftharpoons H_2 + 2S$

Appendix B - Examples of Ni catalysts

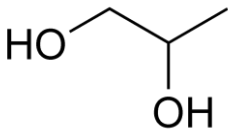
Table B.1 - Comparison between Ni catalysts.

Catalyst	Shape	Particle diameter (nm)	Temperature (°C)	Feed (mL _{CH₄} ·min ⁻¹)	Carbon yield (g _C ·g _{cat} ⁻¹)	Activity (g _{H₂} ·g _{cat} ⁻¹ ·h ⁻¹)	Time (h)	Reference
NiO-CuO/Al ₂ O ₃	-	-	650	400	3.2	0.536	2	[99]
Ni ₃ Al	Fine powder	10	600	25	14.0	2.343	2	[99]
Ni/TiO ₂	Fine powder	31	700	150	15.5	0.862	6	[100]
Ni _{2.7} Cu _{0.3} Al	Fine powder	9	600	5	66.3	2.774	8	[101]
Ni _{2.7} Fe _{0.3} Al	Fine powder	9	600	5	4.0	0.956	1	[101]
Ni/Al ₂ O ₃	Fine powder	11	600	180	15	0.418	12	[102]
NiCo/SBA-15	Fine powder	20	700	250	5.4	0.359	5	[103]
NiO unsupported	-	-	500	20	302.0	3.610	28	[39]

Appendix C - Solvents Properties

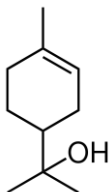
C.1 Propane-1,2-diol

Table C.1 - Propane-1,2-diol properties.

Molecular formula	C ₃ H ₈ O ₂
Molecular structure	
CAS Number	57-55-6
Molecular weight (g·mol ⁻¹)	76.09
Density @ 25 °C (g·cm ⁻³)	1.04
Melting point @ 1 atm (°C)	-59.00
Boiling point @ 1 atm (°C)	188.20
Dielectric constant @ 20 °C	32.0

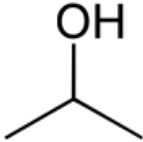
C.2 α -Terpineol

Table C.2 - α -Terpineol properties.

Molecular formula	C ₁₀ H ₁₈ O
Molecular structure	
CAS Number	98-55-5
Molecular weight (g·mol ⁻¹)	154.25
Density @ 25 °C (g·cm ⁻³)	0.94
Melting point @ 1 atm (°C)	18.00
Boiling point @ 1 atm (°C)	219.00
Dielectric constant @ 20 °C	2.8

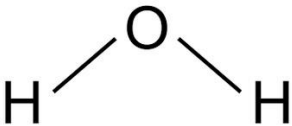
C.3 Propane-2-ol

Table C.3 - Propane-2-ol properties.

Molecular formula	C ₃ H ₈ O
Molecular structure	
CAS Number	67-63-0
Molecular weight (g·mol ⁻¹)	60.09
Density @ 25 °C (g·cm ⁻³)	0.79
Melting point @ 1 atm (°C)	-89.50
Boiling point @ 1 atm (°C)	82.30
Dielectric constant @ 20 °C	18.30

C.4 Water

Table C.4 - Water properties.

Molecular formula	H ₂ O
Molecular structure	
CAS Number	7732-18-5
Molecular weight (g·mol ⁻¹)	18.01
Density @ 25 °C (g·cm ⁻³)	1.00
Melting point @ 1 atm (°C)	0.00
Boiling point @ 1 atm (°C)	100.00
Dielectric constant @ 20 °C	80.40

Appendix D - Granulometric data

D.1 Number

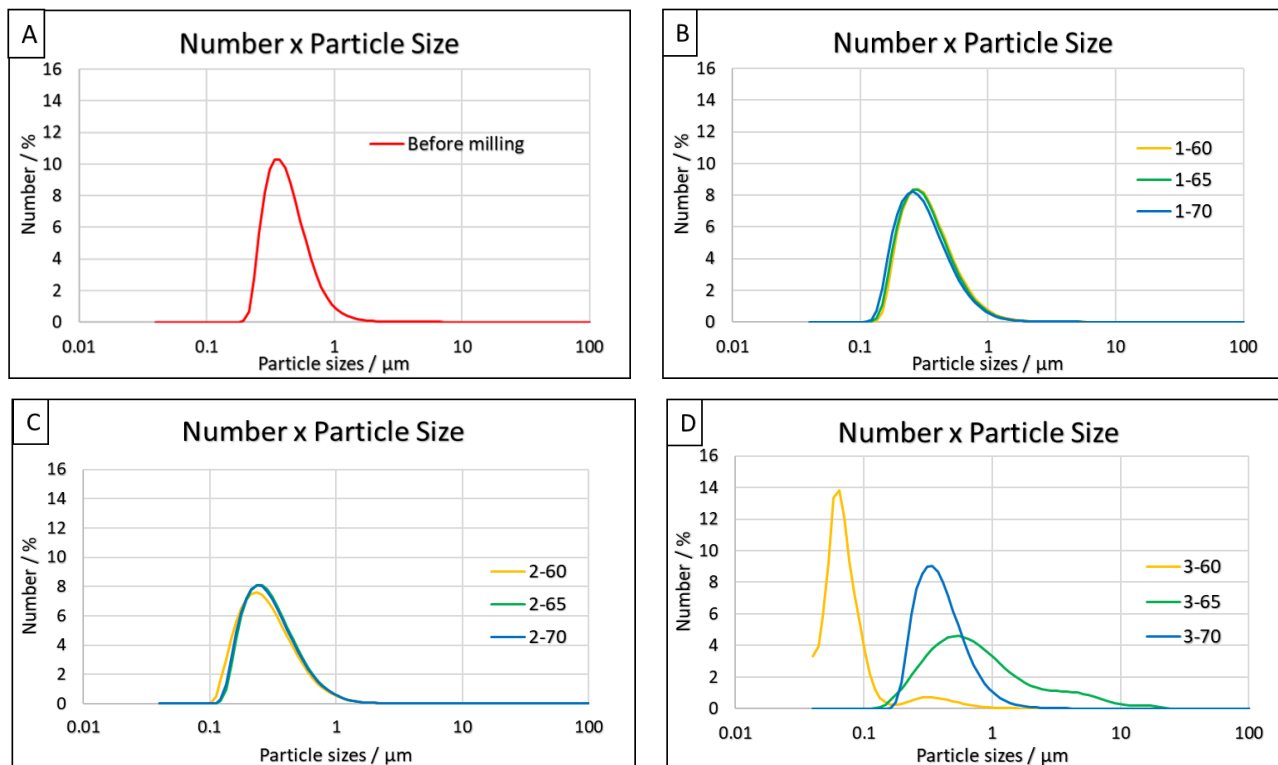
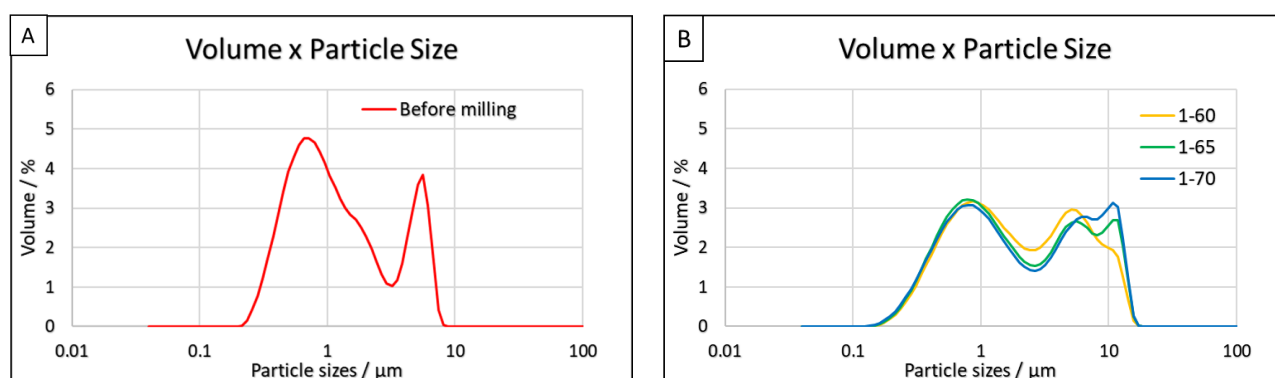


Figure D.1 - Number of particles percentage per particle size for: unmilled catalyst (A); particles that spent 1 h on the ball milling (B); particles that spent 2 h on the ball milling (C); particles that spent 3 h on the ball milling (D).

D.2 Volume



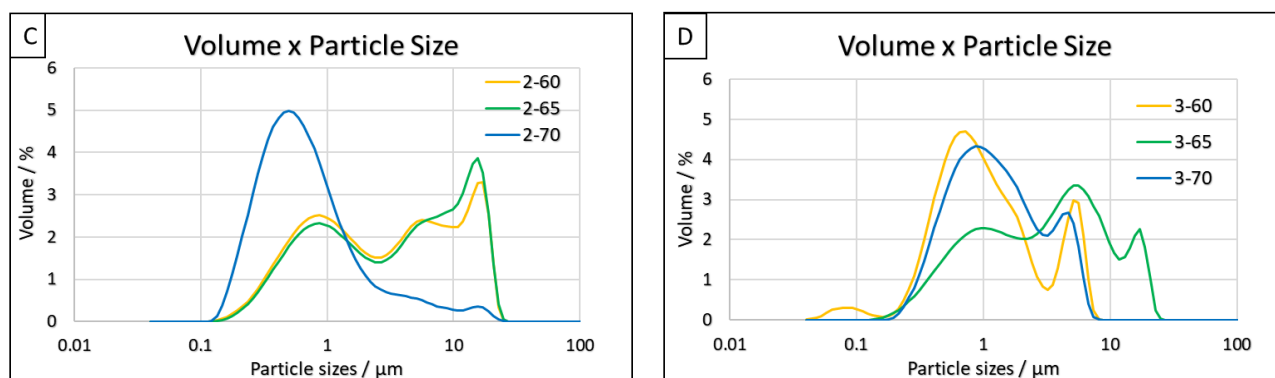


Figure D.2- Volume percentage per particle size for: unmilled catalyst (A); particles that spent 1 h on the ball milling (B); particles that spent 2 h on the ball milling (C); particles that spent 3 h on the ball milling (D).

D.3 Surface Area

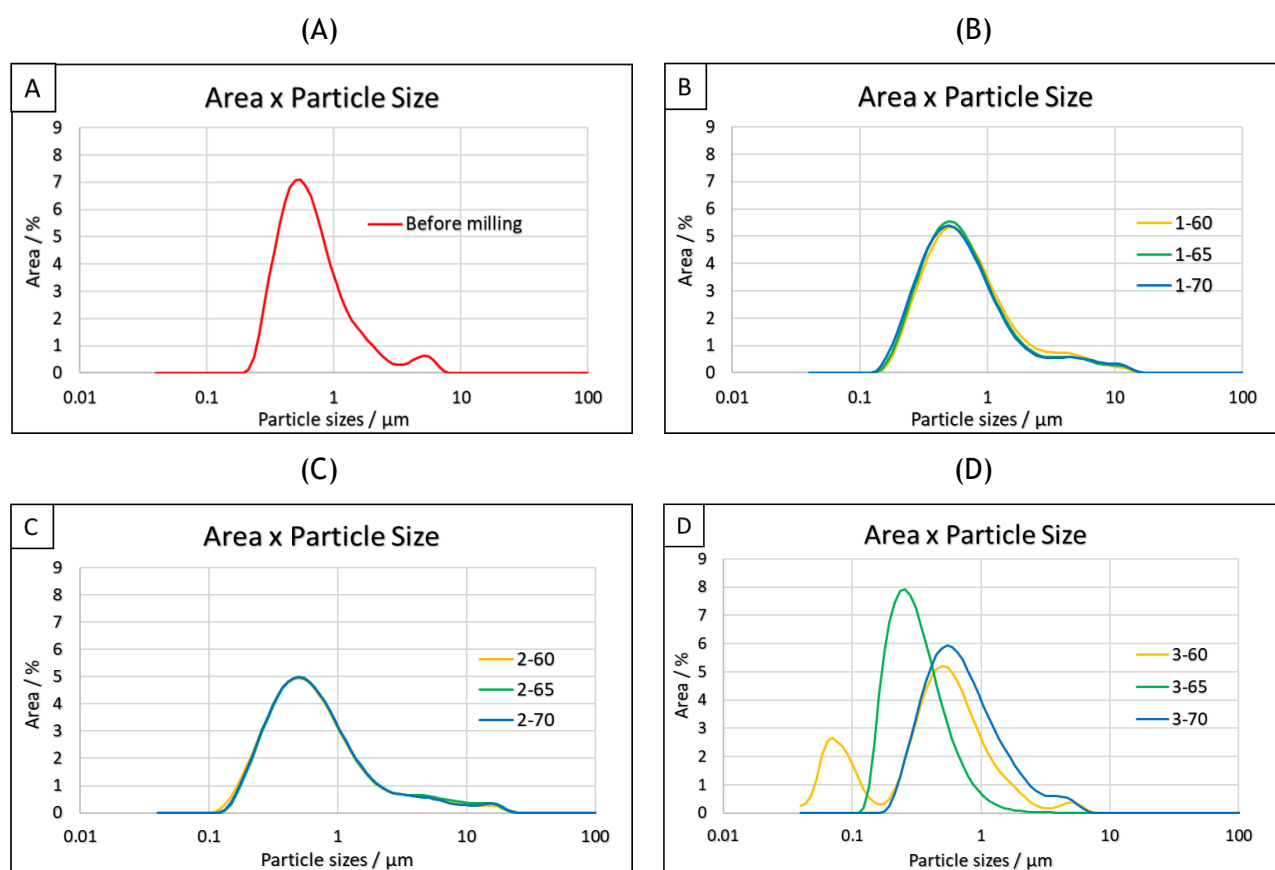


Figure D.3 - Surface area percentage per particle size for: unmilled catalyst (A); particles that spent 1 h on the ball milling (B); particles that spent 2 h on the ball milling (C); particles that spent 3 h on the ball milling (D).

Appendix E - Three Interval Thixotropy Test

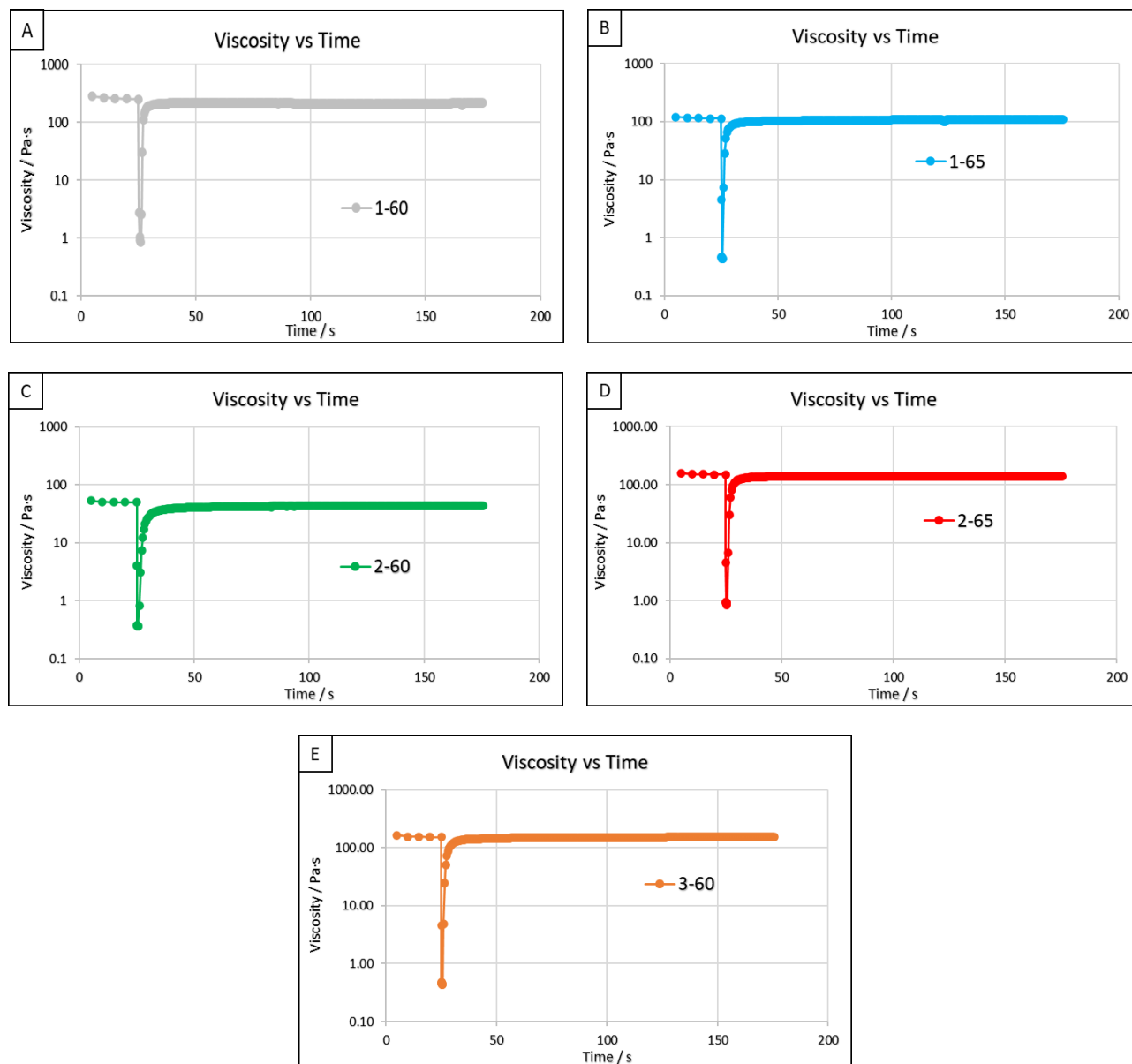


Figure E.1 - Three Interval Thixotropy Test for: (A) 1-60; (B) 1-65; (C) 2-60; (D) 2-65; (E) 3-60.

Appendix F - SEM images and EDS analysis of the screen printed substrates

F.1 Top view and EDS

F.1.1 SP-1.0

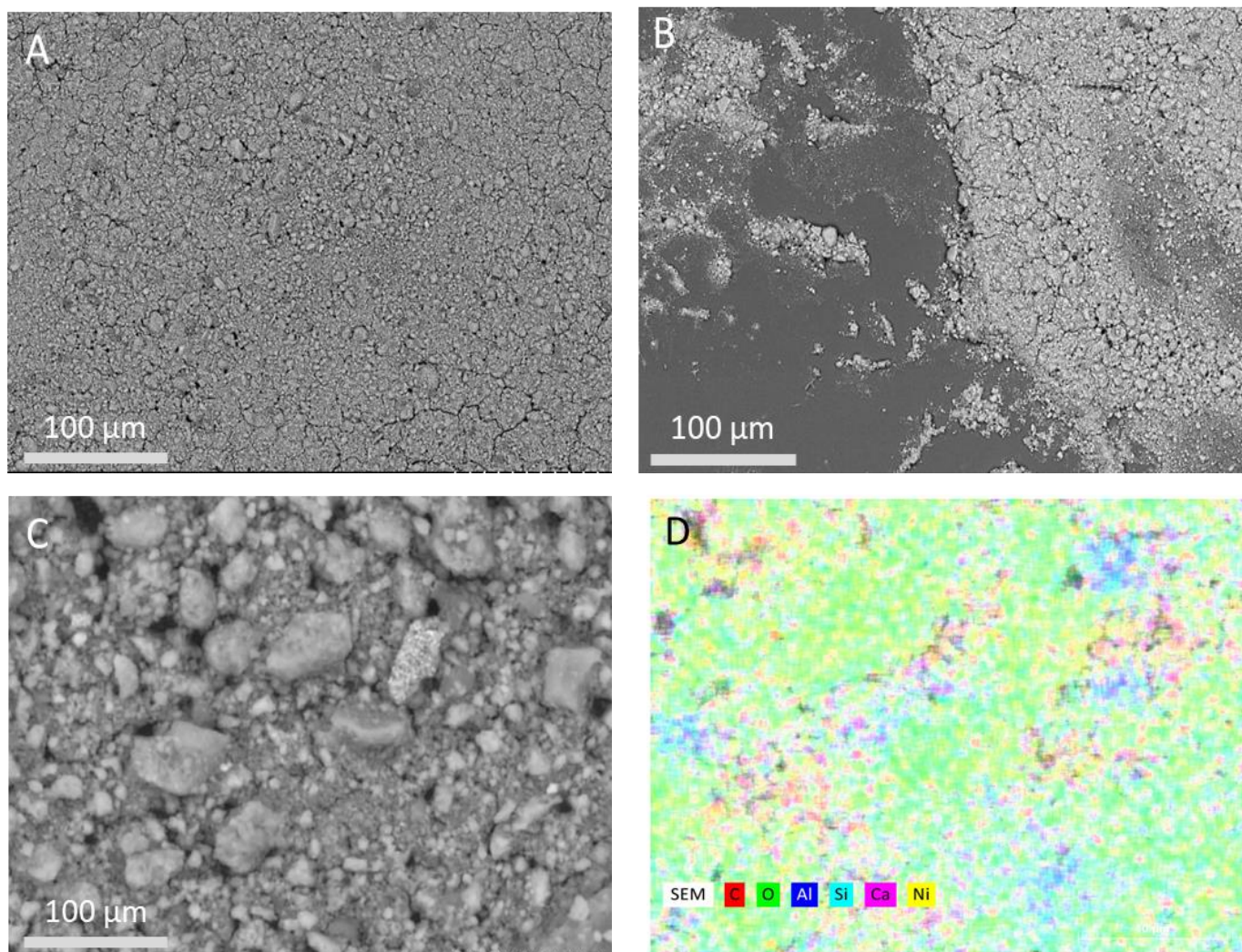


Figure F.1.1 - Top-view SEM images (BSE mode, 15 kV) of the SP-1.0 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure F.1.1.C (D).

Table F.1.1 - Elemental composition obtained from EDS analysis of sample SP-1.0.

Element	O	Ni	C	Si	Al	Ca
Mass (%)	33.02	47.69	5.11	11.04	1.45	1.69
Atom (%)	54.44	21.43	11.22	10.37	1.42	1.11

F.1.2 SP-1.2

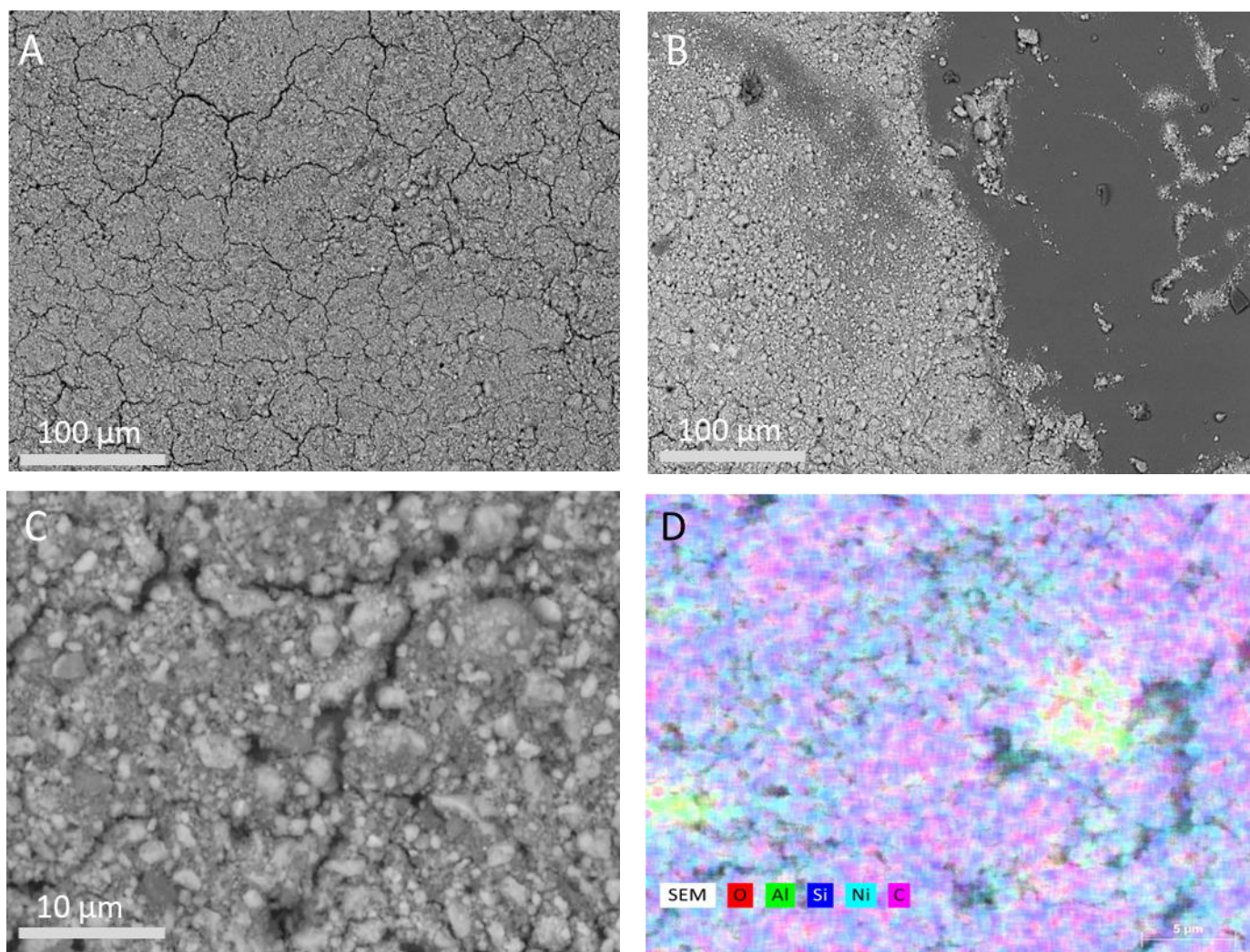


Figure F.1.2 - Top-view SEM images (BSE mode, 15 kV) of the SP-1.2 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure F.1.2.C (D).

Table F.1.2 - Elemental composition obtained from EDS analysis of sample SP-1.2.

Element	O	Ni	C	Si	Al
Mass (%)	29.75	55.50	4.42	8.24	2.10
Atom (%)	52.47	26.68	10.38	8.27	2.19

F.1.3 SP-1.5

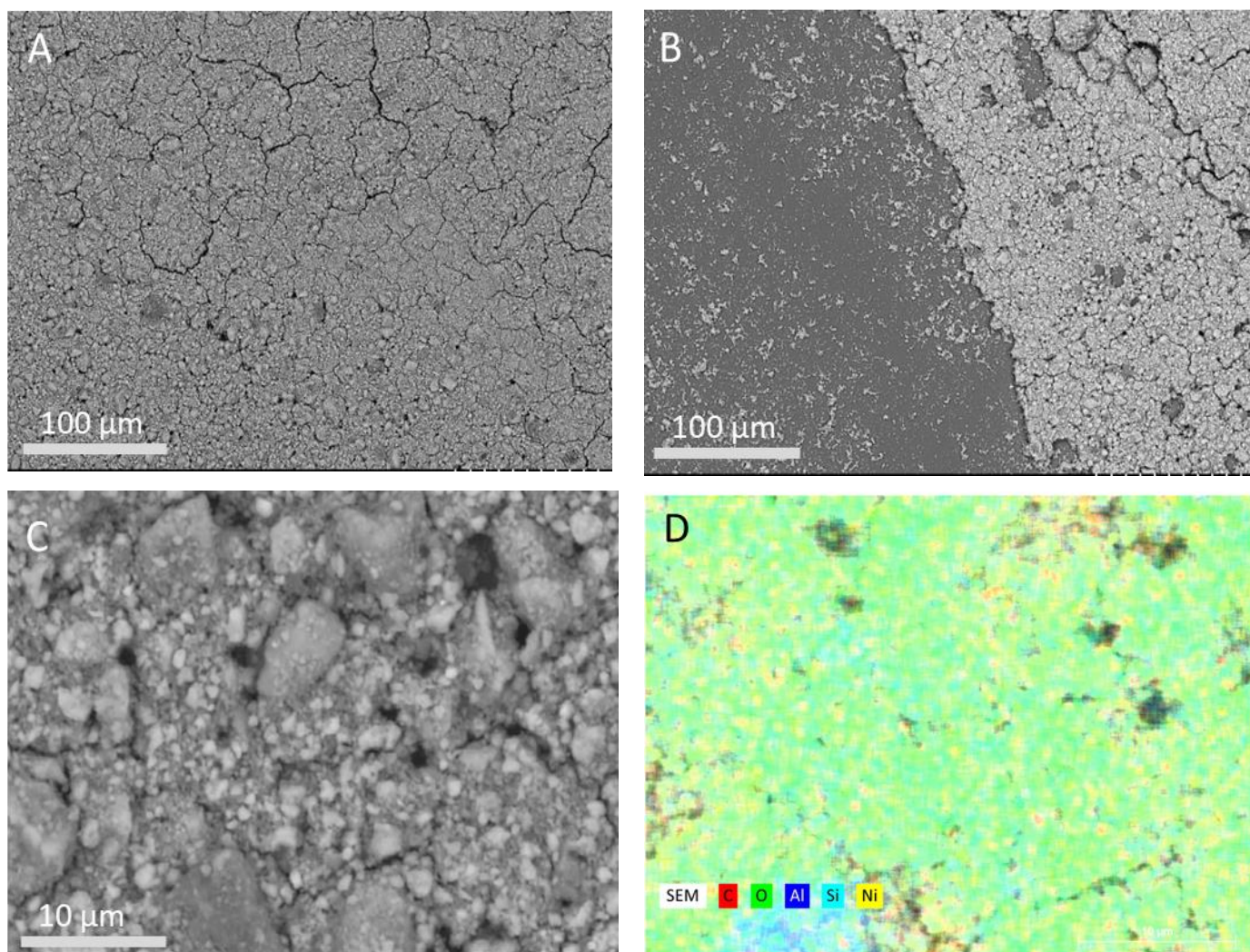


Figure F.1.3 - Top-view SEM images (BSE mode, 15 kV) of the SP-1.5 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure F.1.3.C (D).

Table F.1.3 - Elemental composition obtained from EDS analysis of sample SP-1.5.

Element	O	Ni	C	Si	Al
Mass (%)	32.87	50.99	5.36	8.41	2.37
Atom (%)	54.69	23.13	11.87	7.97	2.34

F.1.4 SP-1.8

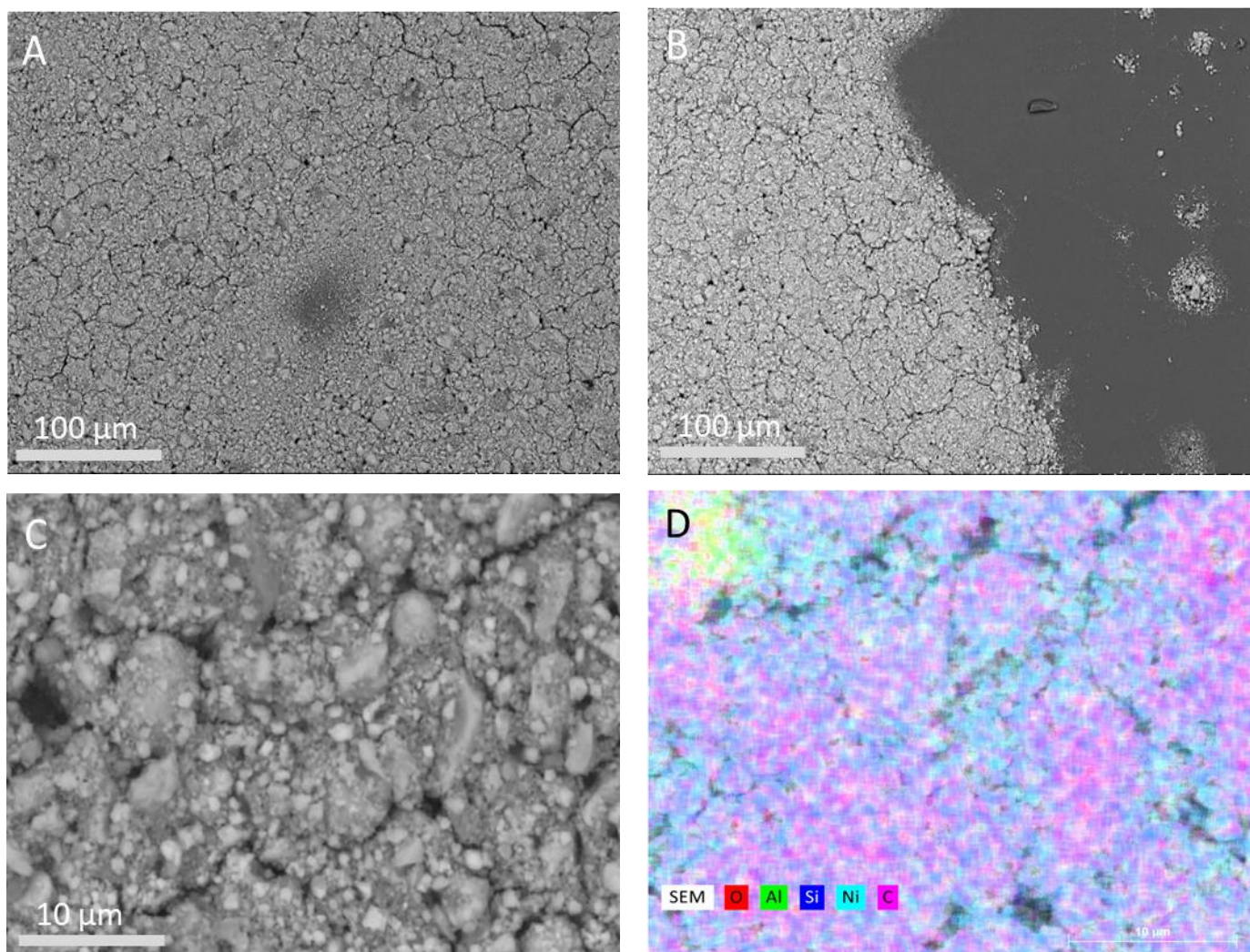


Figure F.1.4 - Top-view SEM images (BSE mode, 15 kV) of the SP-1.8 sample at: the center - x300 (A); the border - x300 (B); and the center - x1000 (C); EDS analysis extracted from figure F.1.4.C (D).

Table F.1.1 - Elemental composition obtained from EDS analysis of sample SP-1.8.

Element	O	Ni	C	Si	Al
Mass (%)	33.37	51.92	5.48	7.73	1.51
Atom (%)	55.51	23.54	12.14	7.32	1.49

F.2 Cross-section

F.2.1 SP-1.0

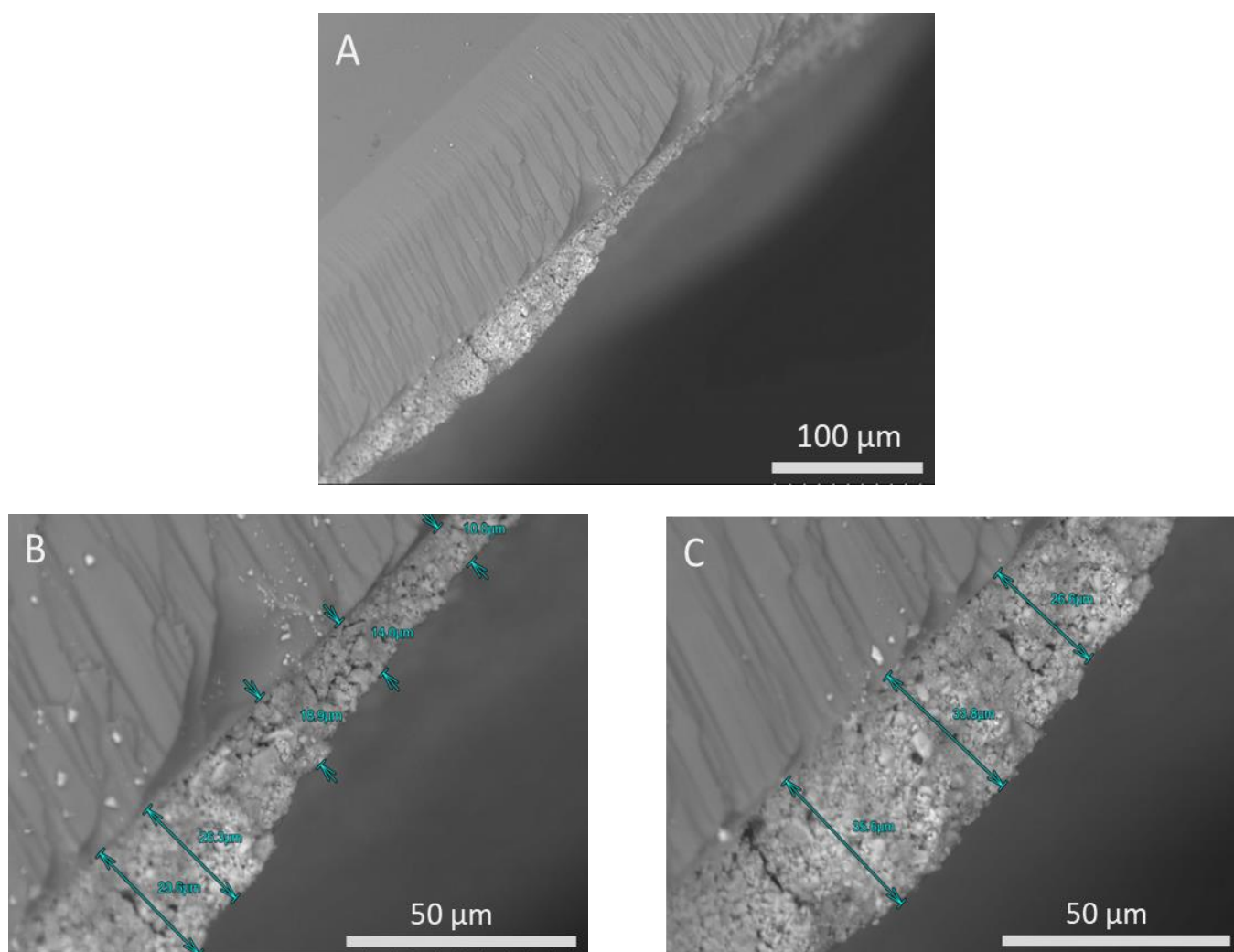


Figure F.2.1 - Cross-sectional SEM images of the SP-1.0 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).

F.2.2 SP-1.2

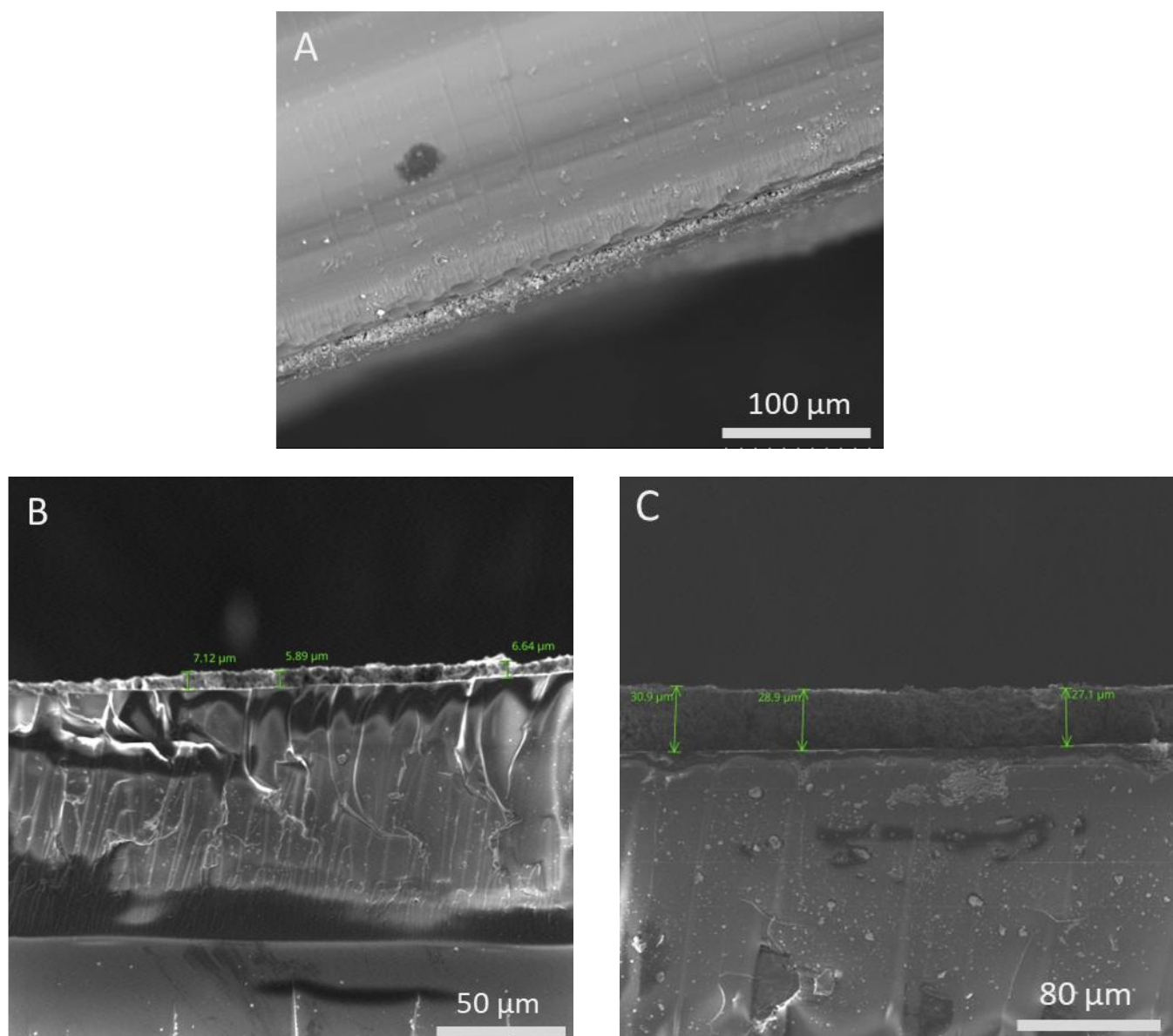


Figure F.2.2 - - Cross-sectional SEM images of the SP-1.2 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).

F.2.3 SP-1.5

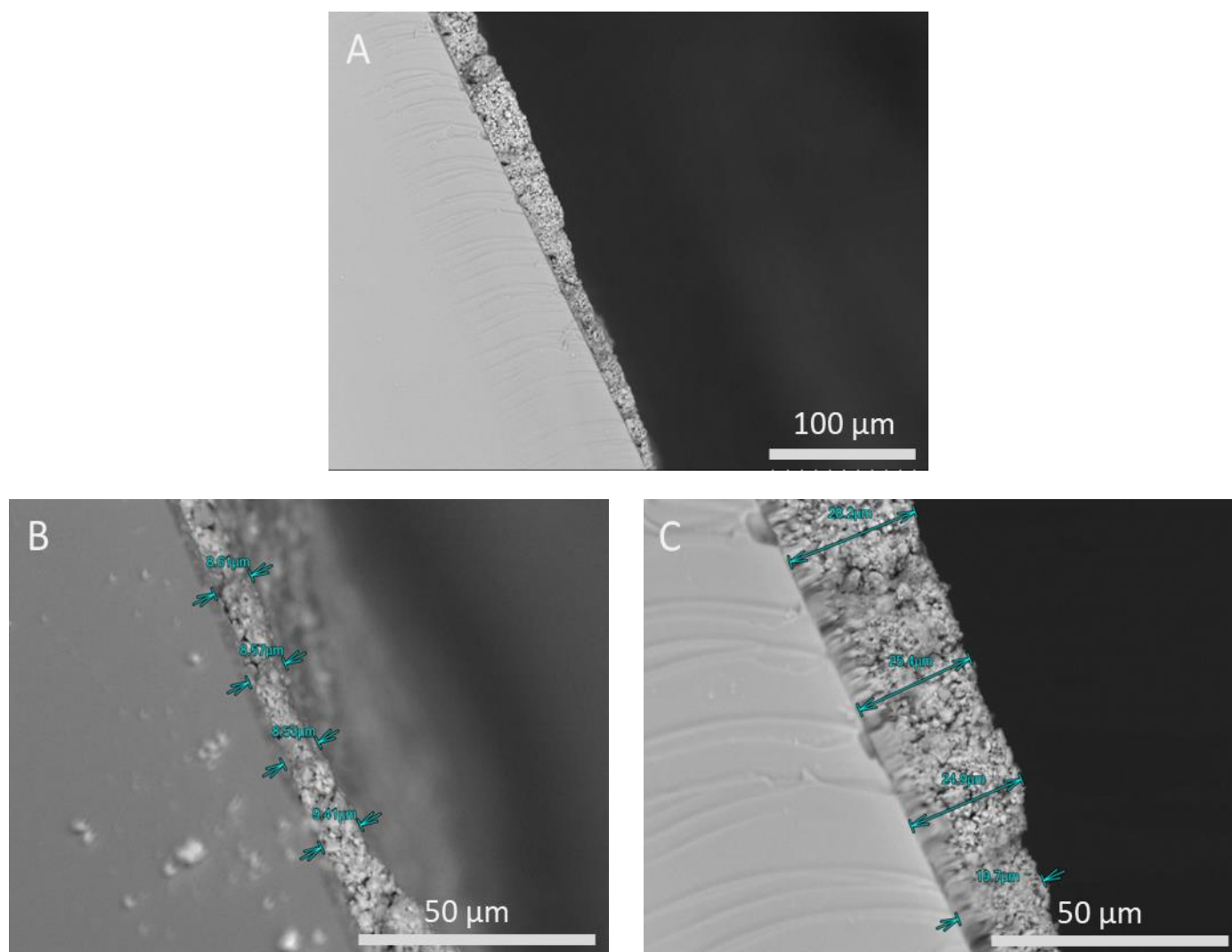


Figure F.2.3 - Cross-sectional SEM images of the SP-1.5 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).

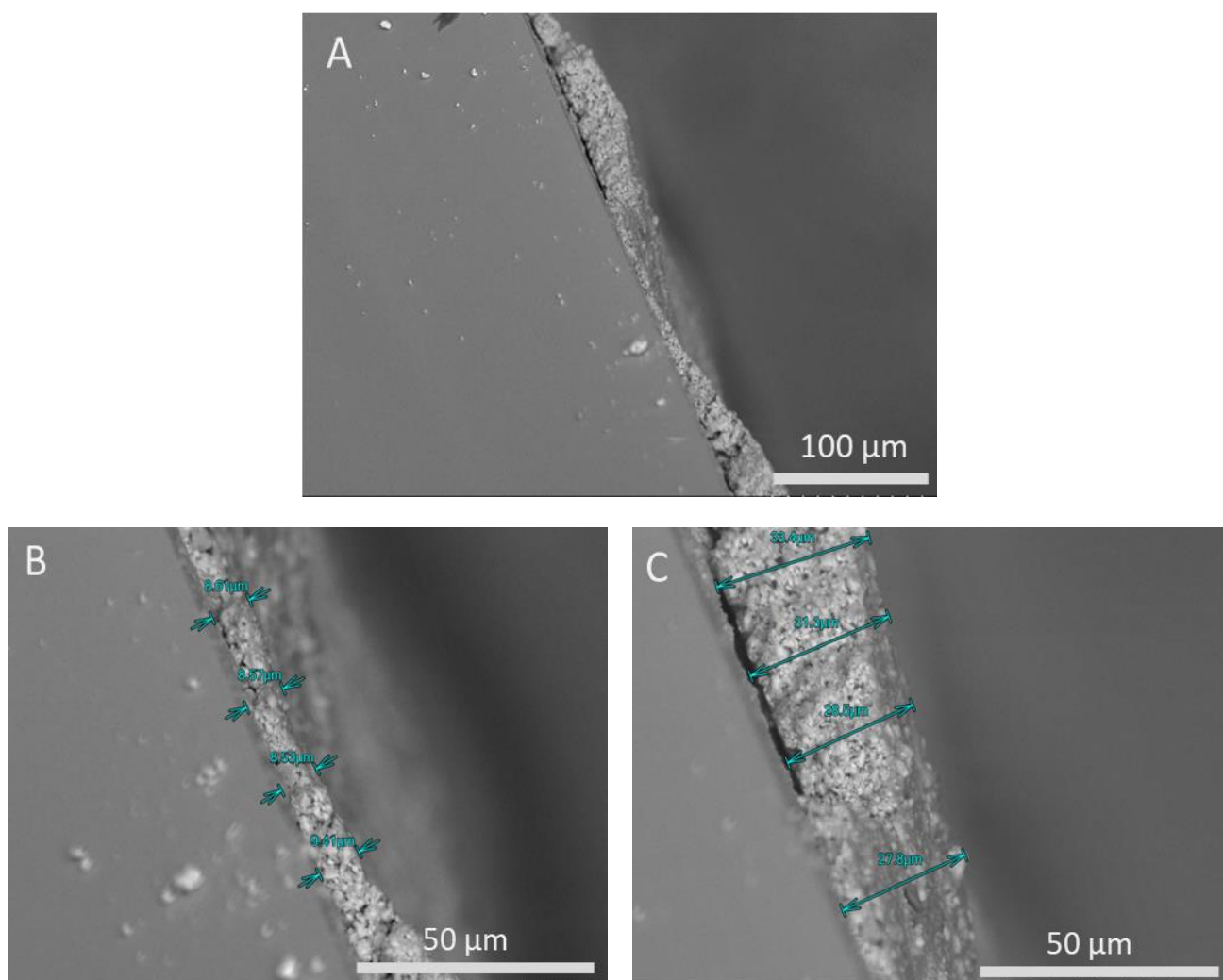
F.2.4 SP-1.8

Figure F.2.4 - Cross-sectional SEM images of the SP-1.8 sample: - x300 (A); and a zoom in from the thinner zone - x1000 (B); and the thicker zone - x1000 (C).

Appendix G - *Post-mortem* SEM images and EDS analysis of the screen printed substrates

G.1 SP-1.0

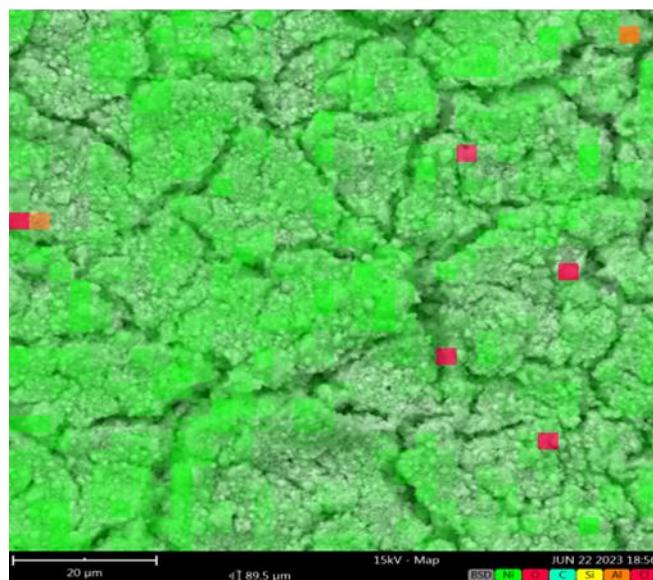


Figure G.1 - Post-mortem EDS analysis of SP-1.0.

Table G.1- Elemental composition obtained from EDS analysis of sample SP-1.8.

Element	O	Ni	C	Si	Al
Mass (%)	14.77	65.50	12.54	5.14	1.36
Atom (%)	27.67	33.45	31.30	5.49	1.51

G.2 SP-1.2

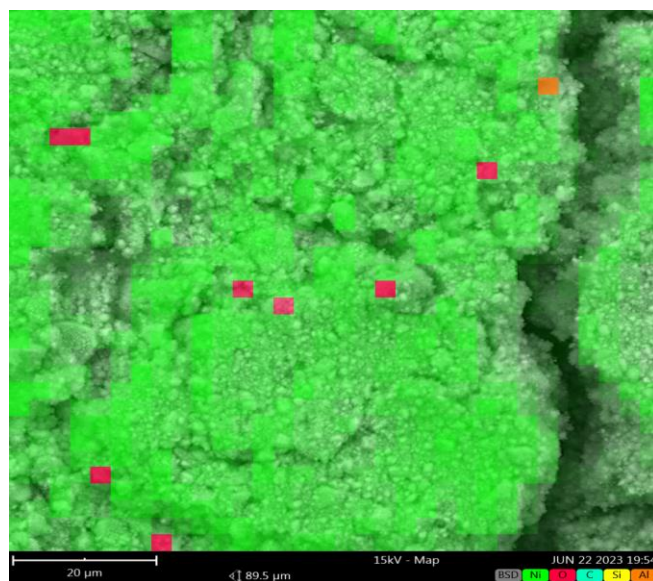
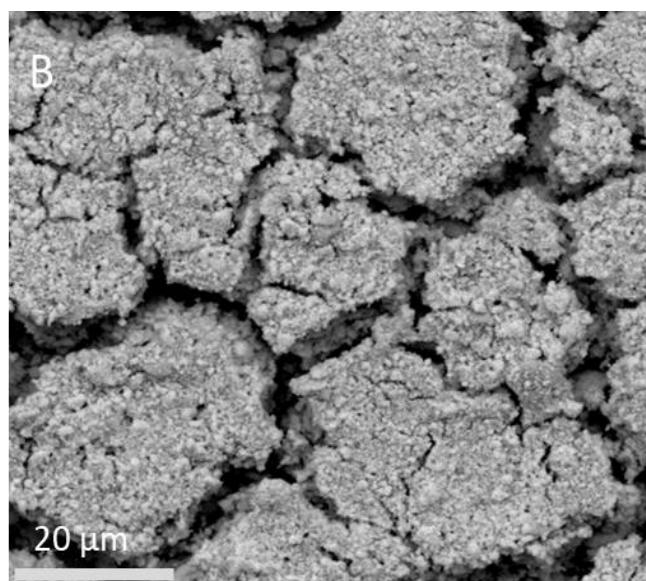
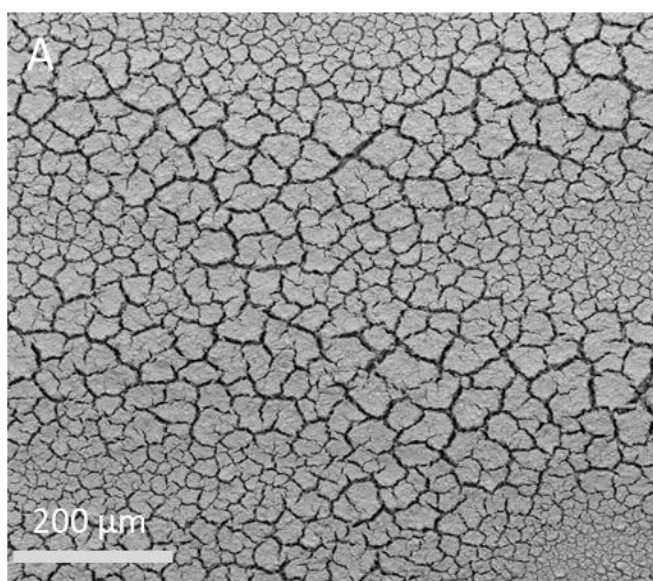


Figure G.2 - Post-mortem EDS analysis of SP-1.2.

Table G.2 - Elemental composition obtained from EDS analysis of sample SP-1.2.

Element	O	Ni	C	Si	Al
Mass (%)	22.51	51.82	19.03	5.33	1.31
Atom (%)	34.22	21.47	38.52	4.62	1.18

G.3 SP-1.5



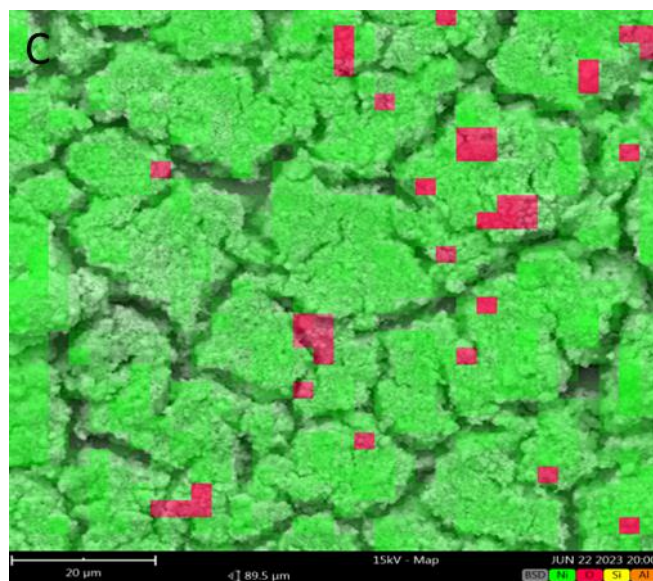


Figure G.3 - Post-mortem SEM analysis of SP-1.5: top-view of the center - x330 (A); top view of the center - x1000 (B); EDS analysis of figure J.4.B (C).

Table G.3 - Elemental composition obtained from EDS analysis of sample SP-1.5.

Element	O	Ni	C	Si	Al
Mass (%)	27.23	63.31	-	7.44	2.02
Atom (%)	54.54	34.57	-	8.50	2.39

G.4 SP-1.8

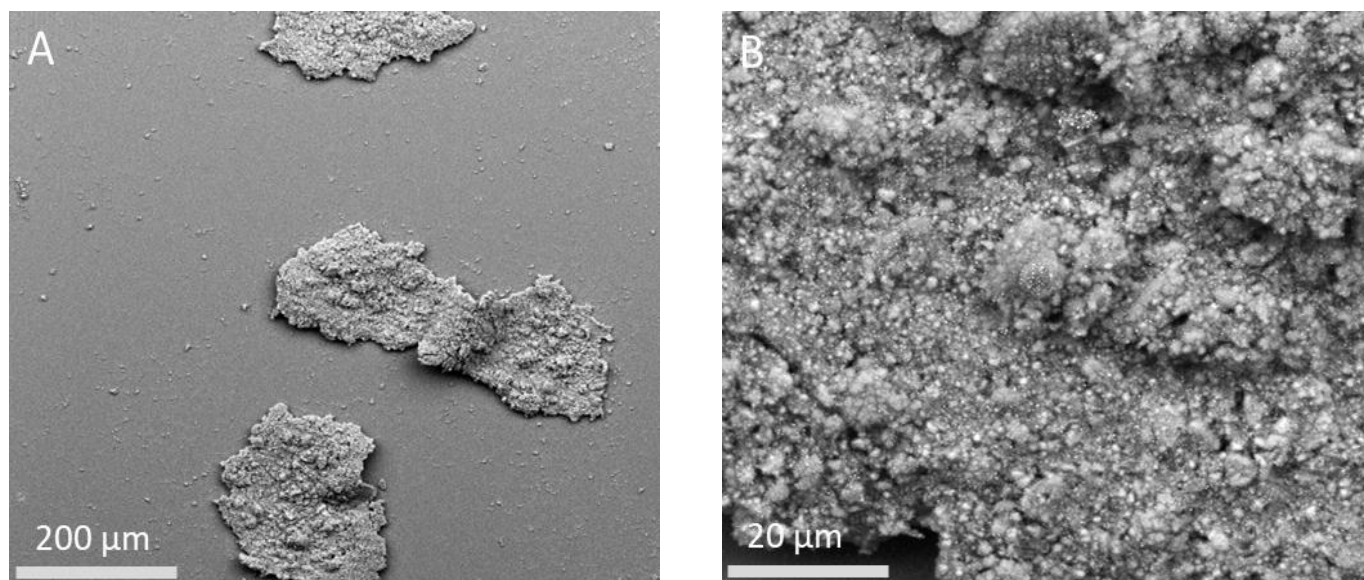


Figure G.4 - Post-mortem SEM analysis of SP-1.8: top-view of the center - x430 (A); top view of the center - x1000 (B).

Appendix H - Regeneration test

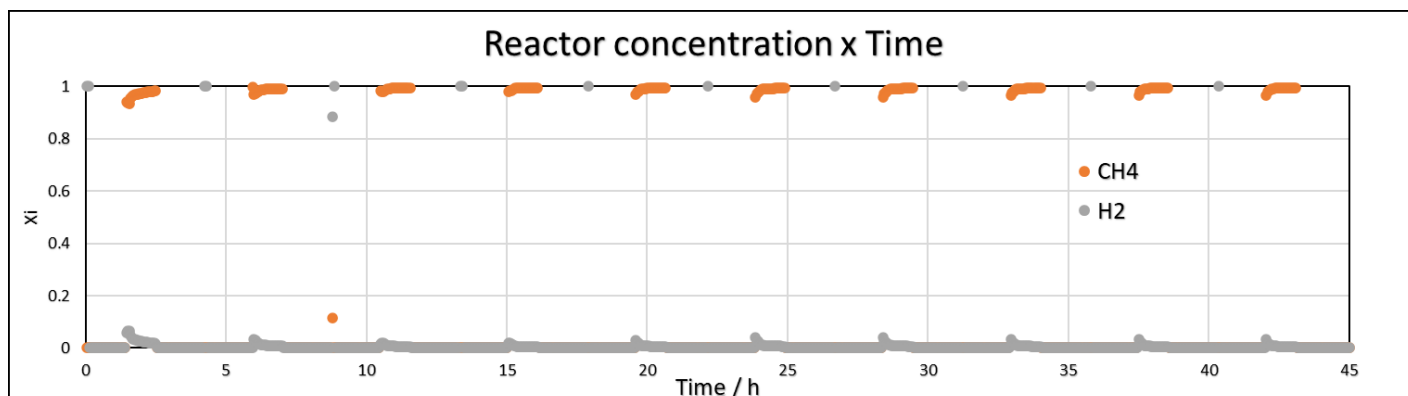


Figure H.1 - Reactor concentration over time during the operation with regeneration.

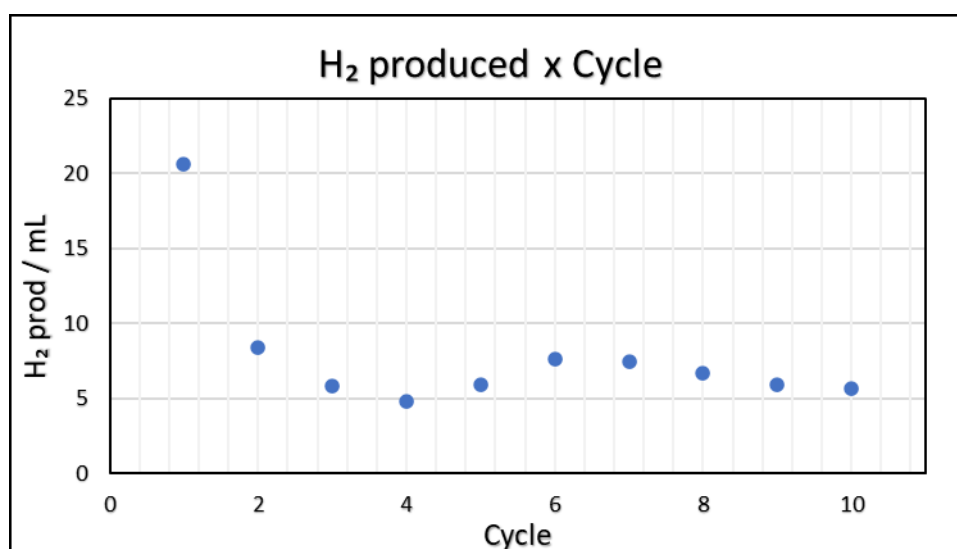


Figure H.2 - Hydrogen production per cycle.

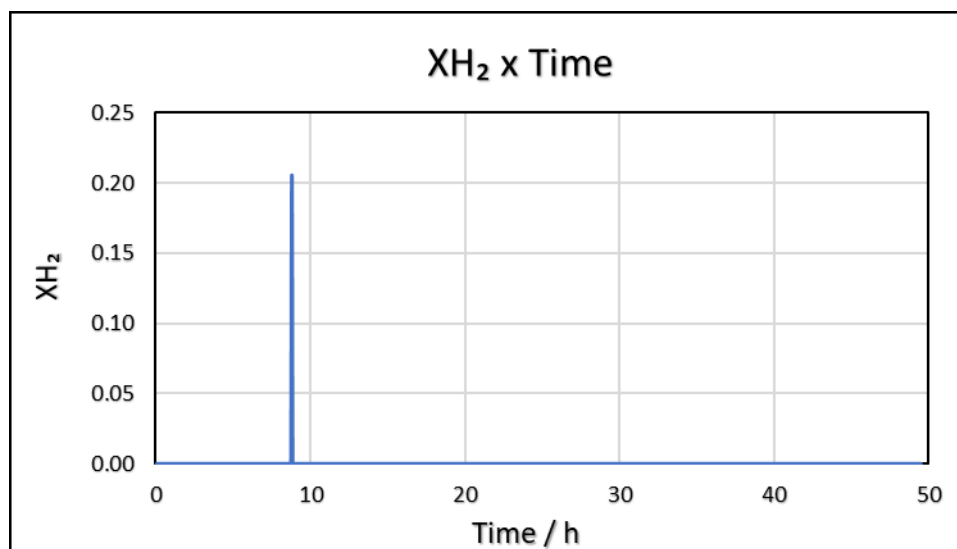


Figure H.3 - Hydrogen conversion during operation.

Appendix I - SEM images and EDS analysis of substrates coated by wet spray

I.1 Top-view and EDS analysis

I.1.1 Spray-2.5

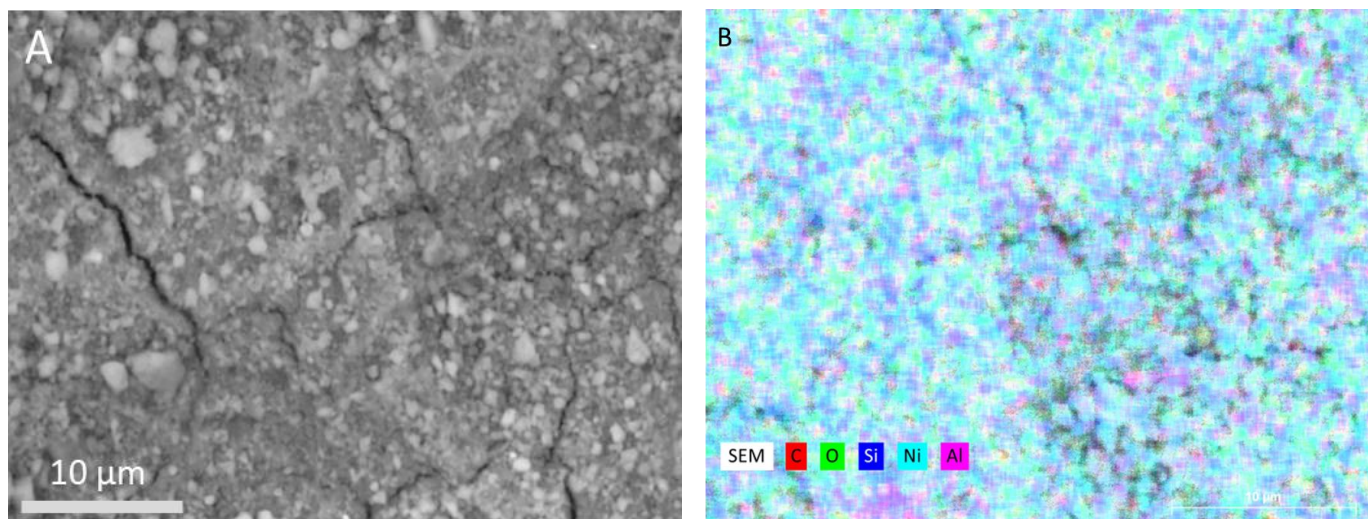


Figure I.1.1 - SEM images of the Spray-2.5 sample: top view of the center - x1000 (A); EDS analysis of figure I.1.1.A (A).

Table I.1.1 - Elemental composition obtained from EDS analysis of sample Spray-2.5.

Element	O	Ni	C	Si	Al
Mass (%)	31.00	50.47	10.12	7.48	0.92
Atom (%)	49.17	21.39	21.39	6.76	0.86

I.1.2 SP-7.5

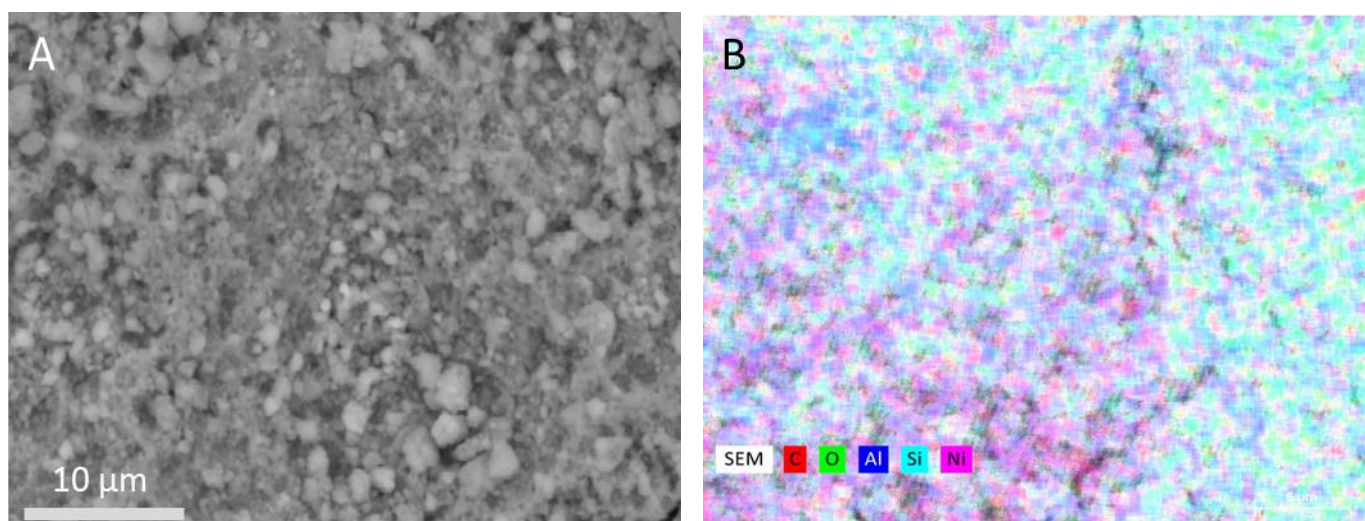


Figure I.1.2 - SEM images of the Spray-7.5 sample: top view of the center - x1000 (A); EDS analysis of figure I.1.2.A (B).

Table I.1.2 - Elemental composition obtained from EDS analysis of sample Spray-2.5.

Element	O	Ni	C	Si	Al
Mass (%)	30.43	52.19	9.00	7.53	0.85
Atom (%)	49.53	23.16	19.51	6.98	0.82

I.2 Cross section

I.2.1 Spray 2.5

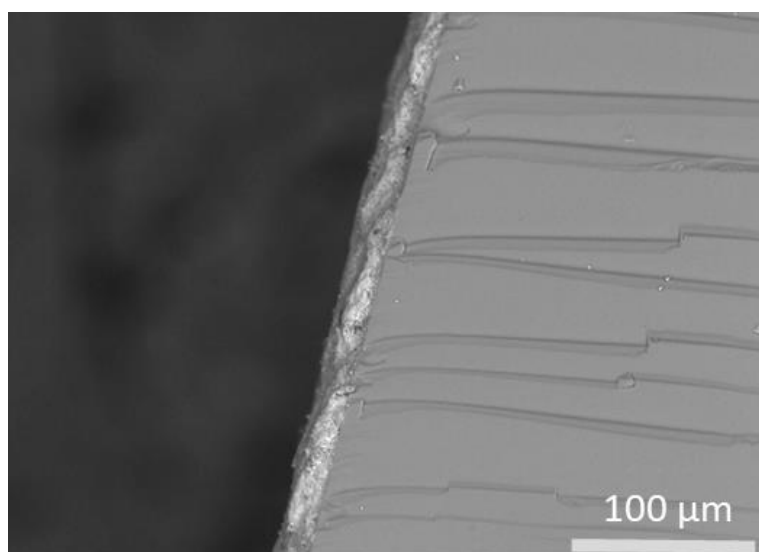


Figure I.2.1- Cross-sectional SEM image of Spray-2.5 sample: cross-section x300.

I.2.2 Spray-7.5

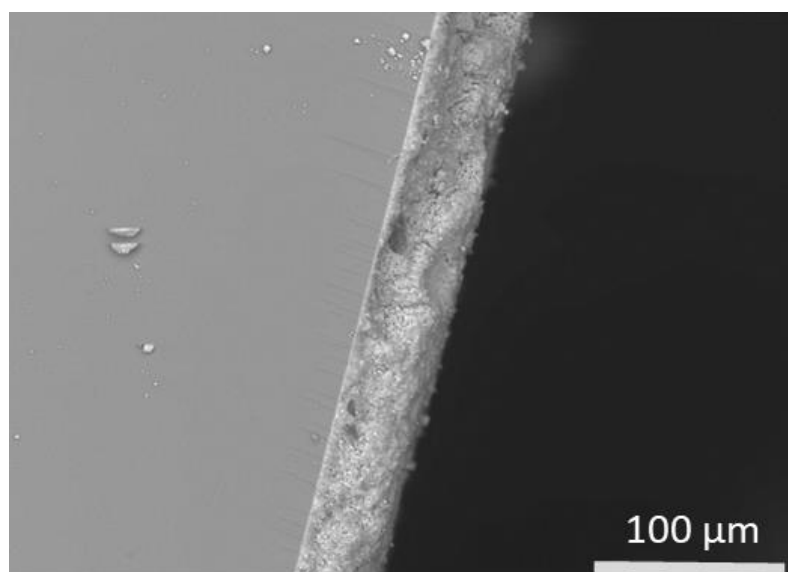


Figure I.2.2 - Cross-sectional SEM images of Spray-7.5 sample: cross-section x300.