Development of catalytic microreactors by plasma processes: application to wastewater treatment

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Citation for published version (APA):
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation

1. Introduction

A key aspect in overcoming the energy and environmental challenges is to improve the efficiency of existing and new processes. As almost all major chemicals are nowadays produced by catalytic processes, an improved efficiency usually entails the optimization of the catalyst and/or reactor. Among such processes, heterogeneous catalysis plays a very active role because of environmental concerns. In order to develop more effective catalytic processes, a better understanding of the reaction pathways and kinetics is needed. However, detailed measurement of the reaction kinetics of fast chemical reactions are often proved difficult, either because the reaction is simply too fast for conventional processes and exceeds typical reactant mixing times, or because the fast reaction kinetics are obscured by a rate-limiting step (the ability of the reactants/reaction products to diffuse to the catalyst surface) that determines the overall reaction kinetics. For this reason, accurate reaction pathways and their associated kinetics still remain largely unknown in the field of catalysis.

Catalytic ozonation is a typical example of this problem. In the field of water and wastewater treatment, chemical oxidation of organic pollutants is one of the major steps of drinking water treatment as it enables the removal of residual organic pollutants that were not eliminated in previous steps. As a trend towards cleaner processes, advanced oxidation processes (AOPs) are becoming more and more attractive. Among the different existing AOPs, the use of ozone is one of the most promising technologies. Indeed, compared to chlorine, the use of ozone
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation as the oxidizing agent exhibits many advantages, since it demonstrates additional antibacterial and antiviral actions [242].

The effective usage of ozone in the above mentioned fields is vital and therefore, extensive research aiming at the utilization of catalytic ozonation has been undertaken [243-245]. Several research groups have reported the high efficiency of catalytic ozonation in the removal of organic contaminants in water [246-252]. However, despite a high number of papers published in this field, there is a lack of understanding of the mechanisms governing catalytic ozonation processes and also deactivation of catalysts.

As a result, catalytic ozonation still remains in the sphere of laboratory experiments with only a few attempts at technological applications. The major problem lies in contradictory mechanisms governing catalytic process proposed by different research groups [253]. Some authors suggest radical pathways involving ozone decomposition and formation of hydroxyl radicals whereas some others indicate that catalytic oxidation proceeds via different pathways, which do not involve hydroxyl radicals.

Another important issue is adsorption of ozone and organics as it is still not clear how, or if, ozone adsorbs on the surface of the catalyst and whether this process leads to ozone decomposition followed by the formation of surface-bound or free radicals. In addition, it is also not known whether adsorption of organics on the surface of catalyst plays a crucial role in the present catalytic process. Several authors reported high adsorption of organic molecules on catalysts whereas others indicated that this process is not required for efficient catalytic oxidation. Therefore, microfluidic devices could be a very useful tool to investigate the mechanism of catalytic ozonation.

The past decade has seen significant advances in the design and use of microfluidic devices to perform chemical analysis and reactions in micron-sized channels and reactors for a broad range of applications in various fields such as physics, chemistry and biotechnology [254-257]. Due to their reduced size and high surface-area-to-volume ratio, such devices offer fast analysis, a high
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation potential for dedicated patterning [258] and short reaction times. The study of reaction mechanisms in microchannels is a promising avenue since the time evolution of products and intermediates reactions can be separated spatially due to the flow in the microchannel [259].

Regarding the type and nature of catalysts that has to be used, nanoclusters of noble metals providing high values of specific surface areas seem to be ideal candidates [260,261]. The most promising method would be to incorporate such catalytic nanoparticles directly onto the wall of a microchannel. Although this has already been attempted, a lowered reactivity due to a small active surface, as well as the leaching of the metals during the chemical reactions were both reported. Therefore, applications of such methods are severely limited [262,263].

To overcome these issues, one possible solution is to decompose ozone in order to produce highly reactive HO• radicals. This can be achieved by the use of catalysts such as ionic metals (e.g. Mn²⁺, Fe²⁺, Fe³⁺, Cr²⁺, Cr³⁺…) in homogeneous catalysis [264] or by the use of noble metals in heterogeneous catalysis [265], the latter of course being preferred from a process point of view. Thus, most heterogeneous catalytic ozonation studies refer to metals supported on powders [266]. Unfortunately, the use of powders requires an extra step of separation in order to retrieve and regenerate the catalyst. Therefore, an immobilized catalyst with a desired lifetime adapted to the process, i.e. that can perform a high number of turnovers, is generally preferred.

In the field of microfluidics, a number of catalytic microreactors [267-269] have recently been developed to immobilize the catalyst by different methods such as “packed-bed” microreactors [270], the insertion of palladium membranes inside microreactors [271] or even the use of polymer brushes to form a polymeric nanostructure enabling the covalently bond of an organic catalyst on the walls of the microreactor [272]. However, given the high price of noble metals, the use of metal oxides is encouraged. In addition, achievement of such catalytic microreactors raises the issue of the nature of the material used for their
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation elaboration. Indeed, for purposes of cost reduction, polymeric-based materials are commonly used in the field of microfluidics.

Nevertheless, these catalysts can’t be coated on such materials using standard methods in light of the fact that these polymers would melt under the high annealing temperature required for the activation of the catalyst. Therefore, Plasma Enhanced Chemical Vapor Deposition (PECVD) processes are one of the techniques that can be used to achieve the deposition of catalytic thin films on such microfluidic materials. Despite the fact that PECVD processes operate at low temperatures, these techniques display many other advantages such as no requirement for solvents and surface activation of catalyst at low temperatures. Indeed, from previous works [273-276], it was demonstrated that plasma processes could lead to the activation of a catalytic coating at low temperatures.

Compared to conventional methods such as impregnation and calcination, the main advantage is that this technique allows structuring the coatings at the micrometric or even the nanometric level what could enhance greatly the catalytic efficiency compared to conventional catalysts [277-280]. In fact, the active phase on the catalyst surface must be highly dispersed over a large specific surface area and the specific activity has to be maximized to ensure an efficient reaction in heterogeneous catalysis. The other advantages are that the chemical composition and the oxidation degree of the metallic elements can be easily tuned by modifying the process parameters such as the gas composition, the discharge power and the treatment time.

The aim of this study is to deposit a thin catalytic layer into a polymer-based microreactor using a Metal-Organic Plasma Enhanced Chemical Vapor deposition process (MO-PECVD). As demonstrated in the previous chapter, Cyclic Olefin Copolymer (COC) appears to be one of the most suitable microfluidic materials which not only can enable rapid prototyping but also withstand plasma processes. It is therefore presently used as the starting material. Regarding the deposition and activation of the catalytic coating, both steps are
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation performed in a single process, i.e., without removing the substrate from the deposition reactor.

Cobalt and iron oxide-based catalysts were chosen for their low cost and ability to catalyze oxidation reactions [281]. Once, the catalytic microreactors obtained, their efficiency are assessed in a catalytic ozonation process. The specific main challenge residing here is the comprehension of the mechanism that governs catalytic ozonation. Studies on the mechanism have mostly been made on relatively simple reactors until now. Unfortunately, there is still a lack of generic model for predicting the efficiency of the catalyst in microreactors.

The present chapter is mainly focused on the preparation and characterization of \( \text{Co}_3\text{O}_4 \) and \( \text{Fe}_2\text{O}_3 \) catalysts using a one-step plasma process as well as their performance in an ozonation process regarding the removal rate of pyruvic acid, catalyst stability and regeneration.

2. Experimental

2.1 Elaboration of the COC microchannels

The first step of the fabrication process of the Cyclic Olefin Copolymer (COC) microchannels is given in Figure 29. COC pellets and thin films (Topas® 6013S-04, \( \text{Tg} = 130 \, ^\circ\text{C}, 254 \, \mu\text{m} \) thick) were purchased from Topas Advanced Polymers. A few grams of the pre-polymerized pellets are placed into an aluminum mold containing the channel design.

![Scheme of the hot embossing step for the elaboration of the blank microreactor.](image)

**Figure n° 29:** Scheme of the hot embossing step for the elaboration of the blank microreactor.
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The mold was fabricated by micromilling (Minitech Machinery, USA) and the feature sizes of the straight microchannel were 15 mm in length, 500 µm in width and 100 µm of depth. The mold used in this study also contained microchannels of 50 mm in length for future studies.

The hot embossing step consists in inserting the mold in a heating hydraulic press (Specac) in which the pellets are consequently melted at 170°C for 10 min. Then a typical pressure of 2 MPa is applied for 10 min in order to obtain chips without bubbles trapped inside the polymer. Finally, after being cooled down to room temperature, the COC plate containing the microchannels is released from the aluminum mold as shown in Figure 30.

![Figure n° 30: Pictures of the hot embossing step for the elaboration of the blank microreactor. From left to right: aluminum mold, COC pellets into the mold, final COC plate obtained.](image)

2.2 Catalysts preparation

Prior to the deposition of both catalysts using the MO-PECVD technique, connection holes were drilled with a 4mm bit and tapped to receive the future plastic connectors. The COC samples were cleaned with ethanol and dried under an argon flow at room temperature. Finally, a shadow-mask was applied on the edges of the channel for future bonding as shown in Figure 31.
Figure n° 31: Scheme of the overview of the elaboration of the catalytic microreactor.

In order to clean off the surface of the samples from adsorbed atmospheric contaminants, the samples were first exposed to a 200 W Argon (150 sccm) / Oxygen (150 sccm) plasma treatment during 10 min for a total pressure of 1.4 mbar.

After this pre-treatment step, a silica layer was deposited in order to increase the adhesion between the catalyst and the surface of the channel but also in order to obtain a homogeneous oxide passivation layer. The silicon oxide thin film was deposited using a homemade low-pressure plasma reactor. The radiofrequency plasma (13.56 MHz) was generated inside a Pyrex tube (46 mm in internal diameter, 600 mm in length) by the use of capacitive coupled external electrodes (Figure 32).

A gas mixture composed of oxygen (300 sccm) and hexamethyldisiloxane (60 sccm) was introduced into the reactor. This system can be used for both liquid and vapor precursors which are introduced into the reactor. The monomer vapors were supplied to the reactor chamber from liquid hexamethyldisiloxane (Merk,
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation. 98.5% ozone was contained in a cylindrical flask, via a heated stainless steel line at 70 °C. A manual valve was used for fine control of the flow. From previous works in our laboratory [162-163], the plasma power and deposition time were respectively of 150 W and 4 min for a total pressure of 1.7 mbar.

Cobalt oxide and iron oxide thin films were deposited using the same reactor with a total pressure of 110 Pa and a glow discharge power of 200 W by the use of a carrier gas (Ar: 300 sccm and O₂: 300 sccm) as shown in Figure 32. The chosen precursor in this process is Octacarbonyl Dicobalt (Strem Chemicals, France) also called cobalt carbonyl Co₂(CO)₈ which is solid under standard conditions. In order to improve the precursor injection into the system, 1 g of the precursor was dissolved in 25 mL of hexene in order to produce fine droplets by the use of an ultrasonic nebulizer. These drops are then evaporated through a heated electro-valve and introduced into the reactor which leads to a pulsed introduction of the precursor in the plasma reactor (t on = 0.9 s, t off = 4 s) for a total treatment time of 720 s. The electro-valve was heated to 70 °C in order to improve the evaporation of the precursor through the introduction line. No heating was applied to the substrate.

The film was deposited on a 2 cm x 2 cm COC film (thickness: 254 µm) previously polished and treated with Ar/O₂ plasma (1:1 ratio) with a total flow rate of 300 sccm and a discharge power of 200 W. The preliminary pre-treatment is carried out to remove eventual adsorbed atmospheric contaminants.
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Figure n° 32: Scheme of the experimental set-up of the MO-PECVD for deposition of Co$_3$O$_4$ and Fe$_2$O$_3$ catalysts.

The Fe$_2$O$_3$ thin film was deposited using the same device as described previously. The main changes here reside in the use of a bubbler instead of a nebulizer and in the application of cycles to avoid the lack of adhesion of the layer onto the sample and therefore, achieve the oxidation step.

The overall catalyst deposition process consists in 6 cycles where a cycle corresponds to a deposition step of 2 mn with Ar and O$_2$ alternated with an oxidation step of 2 mn. The cycle parameters are summarized in Table 12.
Table n°12: Experimental parameters used for the deposition of iron oxide catalysts.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pre-treatment</th>
<th>Deposition step</th>
<th>Oxidation</th>
<th>Post-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>5 mn</td>
<td>2 mn</td>
<td>2 mn</td>
<td>30 mn</td>
</tr>
<tr>
<td>Ar flow rate</td>
<td>150 sccm</td>
<td>200 sccm</td>
<td>-</td>
<td>300 sccm</td>
</tr>
<tr>
<td>O₂ flow rate</td>
<td>150 sccm</td>
<td>100 sccm</td>
<td>100 sccm</td>
<td>-</td>
</tr>
<tr>
<td>Discharge power</td>
<td>150 W</td>
<td>200 W</td>
<td>200 W</td>
<td>150 W</td>
</tr>
</tbody>
</table>

After deposition of the metallic oxides, both samples were post-treated using Ar plasma (300 sccm) at a power of 150 W during 30 mn and compared to stainless steel substrates annealed at 500 °C and 900 °C, respectively for the plasma deposited cobalt and iron oxides. These parameters were chosen in accordance with previous works from our laboratory which demonstrated that the use of an argon plasma lead to more active species and thus, a higher catalytic activity [282].

2.3 Thin films characterization

In order to assess the stability and hydrophilicity of the coated surfaces, water contact angles measurements were performed on the flat coated substrates. Contact angles of MilliQ-water on all substrates were measured using a GBX-3S Digidrop-MCAT instrument. Water droplets of 3 μL in volume were released from a syringe above the sample surface. Images of droplet formation, captured using a high-resolution camera, were analyzed using an image analysis software (Digidrop). For each treatment, contact angle measurements were performed at a minimum of 3 locations on each sample and a typical deviation of ±5° from the mean value was observed. The reported values correspond to the average of these three measurements.

Infrared spectra were carried using a Fourier-Transform Infrared Spectrometer (Cary 660 Spectrometer-Agilent) with an Attenuated Total Reflectance module
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation (GladiATR-Pike). For each spectrum, 44 scans were accumulated with a spectral resolution of 4 cm\(^{-1}\) between 600 and 4000 cm\(^{-1}\).

The surface morphology and thickness of the films were characterized by using a field emission scanning electron microscopy (SEM) (Leica S440) with a 20-300,000x magnification at a resolution of 4.5 nm.

X-ray diffraction (XRD) was performed using a Pan Analytical-X Pert Pro apparatus with a Cu K\(\alpha 1\) radiation source (8027.8 eV) in order to determine whether the plasma deposited films are amorphous or crystalline and in the latter case, measure the crystallites size.

Samples for the transmission electron microscopy investigations were prepared by pouring the dispersed Co\(_3\)O\(_4\) and Fe\(_2\)O\(_3\) particles onto a 300-mesh copper grid using a JEOL JEM 2100F apparatus (JEOL, Japan) operating at an accelerating voltage of 200 kV. Analyses of the crystals were performed on a diffractometer D5000 X-ray using a Cu K\(\alpha 1\) radiation source of 35 kV and the scan was ranged from 10\(^{\circ}\) to 80\(^{\circ}\) with 0.02 steps. The crystallographic nature of the individual particles was indicated by the microdiffraction patterns measured by TEM.

XPS spectra were recorded using a PHI 5600 XPS spectrometer (Physical Electronics, Eden Prairie, USA). Survey and high resolution spectra were acquired using the K\(\alpha\) line of a monochromatic Al (1486.6 eV) and Mg source, respectively, operated at 200 W. Analyses were performed with a 45\(^{\circ}\) angle from the surface. Survey spectra were acquired from 0 to 1400 eV for 15 min. Curve fitting for the high resolution Co\(_{2p}\) and Fe\(_{2p}\) peaks was completed using XPS PEAK Software (version 4.1) by means of a least squares peak fitting procedure using a Gaussian-Lorentzian function and a Shirley baseline fitting. For each sample, three different spots were analyzed and the analyzed surface was evaluated at 0.005 cm\(^2\).
2.4 Chip Assembly

In order to enhance the polymer chain mobility, a mixture of cyclohexane and hexadecane (3:1 volume ratio) was spread on the edges of the COC microchannel to be bonded [283].

The top cover and channel were aligned under an optical microscope and bonded together inside a heated hydraulic press (Specac) at 110 °C for 3 min with a total applied pressure of 0.6 MPa as shown in Figure 33.

![Alignment and Bonding Step](image)

**Figure n° 33:** Scheme of the catalytic microreactor assembly (left). Picture of the sealed catalytic microreactor containing the plasma post-treated cobalt oxide layer (right).

By connecting Teflon tubing (Fisher Scientific) to plastic connectors (F-125H, Fisher Scientific) aligned with the drilled holes of the channel, the solution was then introduced into the catalytic microreactor.

2.5 Adsorption and catalytic activity

The efficiency of the catalytic microreactor was determined by comparing the degradation of a probe pollutant between a blank microreactor (i.e. without catalyst) and the catalytic microreactor; both microsystems having the same dimensions. Catalytic ozonation was studied here by selecting pyruvic acid as the refractory pollutant. Pyruvic acid (PA) was chosen as a probe pollutant since it is known to have low reaction rates with molecular ozone (kO3/AP = 0.13 and 0.98 L•mol⁻¹•s⁻¹ at a pH = 1 and 7 respectively [284]) whereas with hydroxyl radicals, PA has a high reaction rate (kHO•/PA = 1.2×10⁸ L•mol⁻¹•s⁻¹ [285] and hence to pose problems in water purification [286]. In addition, the use of acidic pH prevents the decomposition of ozone [287]. Adsorptions tests were carried by
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation flushing the aqueous solution of PA through the catalytic microreactor without ozone.

2.6 Catalytic ozonation apparatus

![Scheme of the experimental set-up used for catalytic ozonation.](image)

**Figure n° 34:** Scheme of the experimental set-up used for catalytic ozonation.

The catalytic ozonation apparatus showed in Figure 34 consists of an ozone generator (Type COM-AD-01, Anseros) supplied by an oxygen tank. By setting the ozone generator at its full power (29 W) and by the use of a mass flow controller (MFC), ozone is sent to a bubbler containing 20 mL of ultrapure water with pyruvic acid (98%, Alfa Aesar) at a concentration of $0.3 \times 10^{-3}$ mol·L$^{-1}$. The ozone concentration in the liquid phase was followed online using optical fibers (Ocean Optics Maya Pro 2000) with an UV detection set at the wavelength of 259 nm (Deuterium lamp). Considering Beer-Lambert’s law ($\varepsilon_{O_3} = 3300$ L·mol$^{-1}$·cm$^{-1}$) the determined concentration of dissolved ozone was of $0.35 \times 10^{-3}$ mol·L$^{-1}$, when the system reached thermodynamic equilibrium.

In order to have a controlled flow rate of 3.6 mL·h$^{-1}$, a syringe pump (KD Scientific - KDS Legato 210) sucks the solution through the channel and 3.6 mL of the treated solution is recovered in the syringe. The ozone reaction was stopped downstream by adding 130 µL of $10 \times 10^{-3}$ mol·L$^{-1}$ tert-Butanol (99.9%, VWR) solution to rapidly consume any unreacted O$_3$ [288]. The magnetic stirrer ensures the homogenization between the tert-Butanol and the incoming flow arriving in the syringe.
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The percentage of degradation of the catalytic ozonation with both oxides was obtained by measuring the pyruvic acid concentrations before and after reaction using High Performance Liquid Chromatography (HPLC).

2.7 HPLC and FAAS Measurements

Using a Star Varian chromatograph, HPLC analyses were performed in an isocratic mode with 20 µL portion of each treated sample. The initial PA and treated samples were analyzed on a 250 X 4.6 mm Supelcogel H column (Sigma-Aldrich) for organic acids, with acidified Milli-Q water (0.1% Orthophosphoric acid, Sigma-Aldrich) as the eluent, at a flow rate of 0.1 mL·mn⁻¹. The UV detection was set at 210 nm at room temperature in order to analyze organic acids.

In order to assess the stability of such coatings upon catalytic ozonation, analyses of metallic cobalt and iron in solution were performed by Flame Atomic Absorption Spectrometry (FAAS) (Thermo Scientific, Solaar M) with a detection limit of 1 µg·L⁻¹ for both metallic elements.
3. Results and discussion

3.1 Water stability of deposited catalysts

The measured water contact angle on the COC blank surface was equal to 90° whereas the cobalt oxide and iron oxide coated COC films were hydrophilic with a measured water contact angle (WCA) value less than 10°. An aging study was performed by storing the coated samples in air and water for several weeks. The WCA values remained under a value of 10° for up to 2 months, thereby meaning a high wettability for cobalt and iron oxides coatings. The aging study regarding the silica-like coated COC substrates can be found in the previous chapter.

3.2 Deposition of the cobalt oxide catalyst

The chemical bonding structure of the deposited thin film was determined using FTIR-ATR spectroscopy and compared to a stainless substrate annealed at 500°C.
As shown in Figure 35, the FTIR spectra of all deposited samples reveal the presence of 4 main absorption bands. The bands near 1321 cm\(^{-1}\) and 1423 cm\(^{-1}\) were assigned to C-O stretching and C-O-H bending due to the presence of carboxyl groups. This is confirmed by the presence of the C=O stretching band of the carboxyl groups located near 1700 cm\(^{-1}\). The band located at 657 cm\(^{-1}\) is characteristic of the Co-O bond stretching vibration [289]. The large absorption band located between 3000 and 3500 cm\(^{-1}\) is assigned to -OH stretching and corresponds to water adsorption on the surface of the sample. It has to be noted that absorption bands corresponding to the stretching of C-C and C-H are hidden by this large band.

Thus, it can be concluded that cobalt oxide and an organic matrix with carboxyl groups are present on this surface. This organic matrix probably comes from the carbonyl groups contained in the precursor or either from the solvent used during the deposition, as hexene is known to polymerize in plasma processes [290].

Compared to the initial deposited cobalt oxide layer, the plasma post-treated and annealed samples display a more intense Co-O bond stretching band whereas the bands corresponding to carboxyl groups diminish. In addition, the band corresponding to water adsorption tends to narrow when the sample is plasma post-treated or annealed indicating a phase transformation [291].

This phenomenon probably indicates that the polymer matrix formed during the plasma deposition is etched during the argon plasma post-treatment or calcination, leading to a surface exposure of the cobalt oxide, as confirmed by SEM micrographs shown in Figure 36.

From the SEM images, the surfaces of the samples show nearly the same surface morphology with increase in grain size and reveal the presence of nanoclusters having a typical cauliflower-like shape coating which is characteristic of the
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation cobalt oxide layer deposited in similar conditions. The plasma post-treated and annealed samples shown in Figures 36 (b) and (c), exhibit finer nanoparticles on these surfaces than the initial deposited layer (Figure 36 (a)). Moreover, it can be seen that when the sample is post-treated with argon plasma, sharper nanoclusters are formed whereas when the sample undergoes an annealing step, nearly all nanoclusters change to a nano-catkin structure as shown on Figure 36 (f) and in previous works [163]. The cause of such particle refinement is probably due to the ion-bombardment generated in the argon plasma.
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Figure n° 36: SEM images of Co$_3$O$_4$: (a), (b) and (c) are respectively the as-deposited, plasma post-treated and annealed samples. (d), (e) and (f) are the respective magnification of the surface layer.

Ellipsometry measurements were attempted to measure the thickness of the deposited layer. However, the black color of the cobalt oxide layer prevented accurate thickness determination by this technique. Therefore, the thickness of the layer was evaluated by using SEM images taken directly in the coated microchannel as shown in Figure 37.

Figure n° 37: SEM images of plasma post-treated Co$_3$O$_4$ in the COC microchannel: (a) Side view of the layer in the channel and (b) side view of the layer on the inner surface.
From the previous SEM images, it can be seen that the thickness of the plasma post-treated cobalt oxide layer ranges between 3-6 µm in the microchannel while ranging between 700 and 800 nm on the inner surface. In addition, a typical columnar growth due to the crystallization can be observed and was previously proved by Klepper et al [292].

The crystalline structure of the deposited cobalt oxide layer was then investigated using XRD in order to determine the crystallinity of such thin films.

As observed in Figure 38, the crystalline structure was determined by XRD measurements with the catalyst deposited on stainless steel substrates in order to remove the broad features of the amorphous COC patterns (results not shown here). As cobalt oxide can be encountered under three stable phases, XRD patterns for cubic CoO (JCPDS 43-1004), hexagonal Co$_2$O$_3$ (JCPDS 2-770) and spinel Co$_3$O$_4$ (JCPDS 42-1467) were reported here. It can be noted that for all samples, no signals of the silica-like layer were found, which reflects the
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The XRD spectrum of the untreated cobalt oxide thin layer reveals the presence of 4 peaks with three of them located at $2\theta = 43.2^\circ, 50.7^\circ$ and $74.6^\circ$ corresponding to the stainless steel substrate structures [293]. A small peak located at $2\theta = 36.8^\circ$ can be assigned to the [311] lattice plane of spinel Co$_3$O$_4$ [294] or to the [111] lattice plane of cubic CoO. In the case of the plasma post-treated sample, this peak increases whereas another intense peak located at $2\theta = 31.2^\circ$ appears. The latter can be either assigned to the [220] lattice plane of Co$_2$O$_3$ [295] or to the [220] lattice plane of Co$_3$O$_4$.

Besides the peak located at $2\theta = 36.8^\circ$, no other peaks related to the CoO phase was observed, which probably indicates that the cobalt oxide layer undergoes a phase transformation from CoO to the Co$_2$O$_3$ or the Co$_3$O$_4$ phase. However, the intensity of this peak and the presence of peaks located at $2\theta = 19^\circ, 44.8^\circ, 59.4^\circ$ and $65.2^\circ$ respectively corresponding to the [110], [440], [422], [511] and [440] lattice planes of Co$_3$O$_4$ obviously shows the prevalence of this phase. Furthermore, it is still unclear whether the Co$_2$O$_3$ compound exists in a form of a stable crystal.

As for the plasma post-treated sample, the XRD spectrum of the annealed sample display sharper and more intense reflections of the Co$_3$O$_4$ phase. The mean particle size was calculated by applying the following Debye-Scherrer equation [296,297]:

$$D = \frac{K \times \lambda}{\beta \times \cos \theta}$$

- $K$ is the Scherrer constant, a value of 0.9 is generally taken
- $\lambda$ is the X-ray wavelength
- $\beta$ is the full width at half maximum of the peaks
- $\theta$ is the measured angle
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Values of 15 and 10 nm were found for the mean particle size respectively for the as-deposited and plasma post-treated cobalt oxide samples.

However, these XRD analyses do not lead to a definitive assignment as they don’t fully allow discriminating the accurate chemical composition of the annealed or the plasma post-treated samples. Nevertheless, these results demonstrate that cobalt oxide with a preferred crystalline growth orientation is obtained in the layer, and thus, in accordance with the previous SEM observations (Figures 36-37).

![Figure n° 39: XPS High Resolution spectra of Co\textsubscript{2p} for as deposited cobalt oxide layer and plasma post-treated on COC substrates.](image)

As shown in Figure 39, the Co\textsubscript{2p} high resolution spectra was fitted by two components at 780 eV and 796 eV, respectively for the Co\textsubscript{2p}3/2 and Co\textsubscript{2p}1/2 for the as deposited and plasma post-treated cobalt oxide layer samples.
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As reported by Voß et al. [298], the Co_{2p}^{3/2} and Co_{2p}^{1/2} photoelectron lines of Co(II) compounds exhibit a pronounced shoulder on their high energy side (ranging from 784 to 792 eV) which can be assigned to a shake-up process [299]. The satellite peaks in the Co_{2p} spectra are an important signal to discriminate the bonding valence of the cobalt oxide compounds. The lower intensity of the shake-up satellites at 9 eV from the main spin–orbit components of original sample showed that the plasma post-treated cobalt oxide layer was Co_3O_4 and not CoO since its characteristic shake-up peaks are not observed [300-302]. The visible chemical shift occurring for the Co_{2p} peaks indicate that the ionic balance state of Co_{2p} is different for each crystallized Co_3O_4 film [303].

**Table n°13:** Atomic composition of cobalt oxide samples extracted from XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Co (%)</th>
<th>O/Co</th>
<th>C/Co</th>
</tr>
</thead>
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<tr>
<td>As deposited</td>
<td>25.3</td>
<td>50.7</td>
<td>24</td>
<td>2.11</td>
<td>1.05</td>
</tr>
<tr>
<td>Post-treated by argon plasma</td>
<td>20.6</td>
<td>51</td>
<td>28.4</td>
<td>1.79</td>
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</tbody>
</table>

As indicated in Table 13, the atomic content of the samples obtained for the cobalt oxide thin films present traces of neither silicon nor metallic compounds from the silica-like coating or the underlying substrate. The ratio of C/Co decreases when the sample is plasma post-treated, thus indicating that the polymer matrix is being etched by the argon bombardment generated during plasma. In the same way, the O/Co ratio decreases indicating a phase transformation. However, this ratio is higher than the one expected for pure stoichiometric Co_3O_4 (1.33) justified by the presence of carbonyl species. Therefore, it can be concluded that the effect of the argon plasma post-treatment leads to a crystalline phase transformation which is further confirmed by the BET measurements.

From the previous SEM images and possibly assuming that the Co_3O_4 nanoparticles and the pores are in a spherical shape, the mean particle diameter can be estimated according to the following equation:
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\[ d_{BET} = \frac{6 \times 10^3}{\rho \times S_{BET}} \]

- \( d_{BET} \) is the average diameter of a spherical particle (in nm)
- \( \rho \) is the theoretical density of \( \text{Co}_3\text{O}_4 \) (6.11 g/cm\(^3\))
- \( S_{BET} \) is the specific surface area of the catalyst layer (in m\(^2\)/g)

The average pore diameter can be calculated from the Barret-Joyner-Halenda (BJH) adsorption method [304], given by the following equation:

\[ d_{pore} = \frac{4 \times V_{pore} \times 10^3}{S_{BET}} \]

- \( d_{pore} \) is the mean diameter of a spherical pore (in nm)
- \( V_{pore} \) is the pore volume (in cm\(^3\)/g)
- \( S_{BET} \) is the specific surface area of the catalyst layer (in m\(^2\)/g)

As shown in Table 14, the BET surface increases from 85 m\(^2\)/g for the as deposited cobalt oxide layer to 104 m\(^2\)/g for the argon plasma post-treated sample, thus confirming the expected crystallization effect of the argon plasma post-treatment. In addition, the estimated average pore size decreases with the plasma post-treatment at a lower value than the mean diameter size of the particle.

The mean particle sizes calculated from the surface area data are 11 nm and 9 nm respectively for the untreated and plasma post-treated samples; values which are in good agreement with the XRD results.

However, regarding the deposited silica layer, calculations from the BET measurement and estimated from the BJH methods indicate an average pore diameter of 5.4 µm with a mean particle size of 7.1 µm. These values are most probably inaccurate as the previous BJH equation is applicable to microporous and mesoporous materials, and thus not applicable to the deposited silica-like layer due its low specific surface area value (0.4 m\(^2\)/g).
Table n°14: BET measurements of cobalt oxide deposited by MO-PECVD on COC substrates with a silica-like underlayer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Total Developed Surface Area / Geometric surface Ratio</th>
<th>Average pore diameter (nm) (^a)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Mean particle size (nm) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited SiO(_2)</td>
<td>0.4</td>
<td>700</td>
<td>5400</td>
<td>0.52</td>
<td>7100</td>
</tr>
<tr>
<td>As deposited Co(_3)O(_4)</td>
<td>85</td>
<td>3300</td>
<td>11</td>
<td>0.23</td>
<td>11</td>
</tr>
<tr>
<td>Deposited Co(_3)O(_4) post-treated by Ar plasma</td>
<td>104</td>
<td>3800</td>
<td>8</td>
<td>0.21</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^a\) Estimated by the BJH method

\(^b\) Calculated from the BET measurements

3.3 Deposition of the iron oxide catalyst

On the FTIR spectrum of the iron oxide coated sample, as shown in Figure 40, a characteristic band of the Fe-O bond stretching can be found at 670 cm\(^{-1}\) [305,306]. The bands near 1100 cm\(^{-1}\) and 1500 cm\(^{-1}\) were respectively assigned to C-O stretching and C=O stretching due to the presence of carboxyl groups. The absorption bands located at 2945 cm\(^{-1}\) and 2867 cm\(^{-1}\) are assigned to the carbon/hydrogen stretching vibration modes of -CH\(_2\) and -CH\(_3\) groups from the polymer backbone. For all the substrates, the band located between 2340 cm\(^{-1}\) and 2360 cm\(^{-1}\) is assigned to the CO\(_2\) elongation. The large absorption band located between 3000 and 3500 cm\(^{-1}\) is assigned to -OH stretching, due to water molecules being adsorbed just like for the cobalt catalyst spectrum. Here again, we can conclude that iron oxide and an organic matrix with alcohol and carboxyl groups are present on the surface.
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**Figure n° 40**: FTIR spectra of iron oxide as deposited (red line), post-treated by argon plasma (green line), plasma deposited then annealed (red line).
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Figure n°41: SEM images of plasma deposited iron oxide. Plane views of a) as deposited b) post-treated by argon plasma, c) annealed at 900 °C; d), e) and f) are the corresponding side views.

SEM micrographs displayed in Figure 41 reflects the effect of the plasma post-treatment on the coated surface. The surface of the thin films presents the same
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classic columnar growth with a cauliflower-like shape morphology. As for the cobalt oxide layer, due to the pronounced red color of the deposits, the thickness of the layer was evaluated from the SEM micrographs and ranges between 5 and 6 µm.

Figure n°42: XRD patterns of the deposited iron oxide coatings. Patterns are shifted vertically for better visualization.

From the XRD patterns of the iron oxide coatings shown in Figure 42, the plasma deposited iron oxide layer appears. XRD patterns of the polymorphs of Fe₂O₃. It has to be noted that the magnetite Fe₃O₄ XRD pattern is very similar to the maghemite (γ-Fe₂O₃) one. The as-deposited iron oxide and plasma post-treated sample present similar peaks (2θ= 30°, 32°, 35°, 44°) than the hematite (α-Fe₂O₃) phase.

However in the case of the post-treated sample, small peaks appearing at 2θ= 33° and 44° indicates the presence of the maghemite phase (γ-Fe₂O₃). We can possibly assume that a mixture of these two phases occur during the plasma post-treatment whereas for the annealed sample, it can clearly be seen that it is the hematite phase which occurs on the surface.
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By applying the Debye-Scherrer equation, values of 50 and 40 nm were found for the mean particle size respectively for the as-deposited and plasma post-treated iron oxide samples. Moreover, due to this high size values compared to the cobalt oxide samples, we can assume that the iron oxide layer didn’t undergo a high crystallization rate.

![Figure n°43: TEM micrographs of plasma post-treated iron oxide.](image)

Indeed, from the TEM micrographs shown in Figure n°43(a) and (b), two phases seem to appear on the surface of the iron oxide surface treated by argon plasma. Crystallized nanoparticles of iron oxide having a hexagonal form, which are represented by dark dots in the bright-field micrograph (Figure 43(a)) and by white dots on the dark-field micrograph (Figure 43(c)), appear along nanoparticles having an intermediate shape between an amorphous structure and a tetragonal crystalline one.
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Moreover, it can be clearly seen that these nanoparticles aggregate and stack on each other. The hexagonal crystalline structure clearly indicates the presence of α-Fe$_2$O$_3$ whereas γ-Fe$_2$O$_3$ has a tetragonal crystalline structure [307]. The average size of the nanoparticles was estimated to 10 nm.

By using the diffraction mode, the values of the diffraction angles were determined to be 30°, 35° and 44° (2θ) which clearly indicate the presence of γ-Fe$_2$O$_3$ [308,309].

![Figure 44: XPS High Resolution spectra of the iron oxide layer as deposited by MO-PECVD, argon plasma post-treated and annealed samples.](image)

As shown in Figure 44, the iron oxide samples were fitted with two main peaks: Fe$_{2p}$3/2 (711 eV) and Fe$_{2p}$1/2 (725 eV) [310]. The XPS spectrum of the annealed sample was reported here in order to understand the effect of the argon plasma post-treatment, as to the best of our knowledge, no comparison between both activation techniques were reported in the literature. Regarding the annealed sample, the clear presence of a satellite peak (719 eV) confirms the iron oxide phase to be α-Fe$_2$O$_3$ as it corresponds to the characteristic shake-up peak observed for Fe$^{3+}$ in α-Fe$_2$O$_3$ [311].
These results are in accordance with the fact that the phase transformation of the \( \gamma\text{-Fe}_2\text{O}_3 \) phase to the \( \alpha\text{-Fe}_2\text{O}_3 \) one occurs at high temperatures (above 400°C) \[312\]. Therefore, as for the cobalt oxide layer, the argon plasma post-treatment enables here the substitution of the calcination step by inducing a phase transformation and a surface refinement of the plasma deposited layers.

**Table n°15:** Atomic contents of plasma deposited iron oxides on COC substrates extracted from XPS for the as-deposited and argon plasma post-treated sample, on stainless steel substrate for the annealed sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>Cr (%)</th>
<th>O/Fe</th>
<th>C/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>22.9</td>
<td>55.3</td>
<td>21.8</td>
<td>-</td>
<td>-</td>
<td>2.54</td>
<td>1.05</td>
</tr>
<tr>
<td>Post-treated by argon plasma</td>
<td>17.5</td>
<td>58.1</td>
<td>24.4</td>
<td>-</td>
<td>-</td>
<td>2.38</td>
<td>0.71</td>
</tr>
<tr>
<td>Annealed at 900°C</td>
<td>11.9</td>
<td>60.2</td>
<td>7.6</td>
<td>4.7</td>
<td>15.6</td>
<td>7.92</td>
<td>1.56</td>
</tr>
</tbody>
</table>

As indicated in Table 15, when the sample undergoes argon plasma post-treatment, the atomic percentage of iron increases from 21.8 % to 24.4% whereas the carbon content decreases. The O/Fe ratio passes from 2.54 to 2.38 leading towards a ratio of an ideal \( \text{Fe}_2\text{O}_3 \) layer (1.5). However, for the annealed sample, atomic contents of manganese and chromium were identified. The latter appear on the surface of the sample due to their migration from the stainless steel substrate. Indeed, the calcination temperature is close enough to the processing temperature of stainless steel (1000°C).

Therefore, the effect of the plasma post-treatment cannot be compared to the effect of calcination. Nevertheless, from the previous characterization results, it can be assumed that the argon plasma post-treatment leads to a crystallization of the initial deposited layer in the same way as for the cobalt oxide layer.

BET measurements for the as deposited and plasma post-treated iron oxide coatings were reported in Table 16.
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Table n°16: BET Measurements for iron oxide deposited by plasma (as deposited and plasma post-treated).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Total Developed Surface Area / Geometric surface Ratio</th>
<th>Average pore diameter (nm) (^a)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Mean particle size (nm) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited SiO(_2)</td>
<td>0.4</td>
<td>700</td>
<td>5400</td>
<td>0.52</td>
<td>7100</td>
</tr>
<tr>
<td>As deposited Fe(_2)O(_3)</td>
<td>26</td>
<td>3600</td>
<td>64</td>
<td>0.41</td>
<td>44</td>
</tr>
<tr>
<td>Deposited Fe(_2)O(_3) post-treated by Ar plasma</td>
<td>35</td>
<td>4900</td>
<td>41</td>
<td>0.36</td>
<td>33</td>
</tr>
</tbody>
</table>

\(^a\) Estimated by the BJH method  
\(^b\) Calculated from the BET measurements

Compared to the Co\(_3\)O\(_4\) thin film samples, the measured BET of the iron oxides samples before and after the plasma post-treatment present a value of approximately 4 times. In the same way, the average pore diameter and mean particle size are at least 3 times greater. This is probably due to the non-fully crystallized particles present on the surface of the layer; assumption which is in accordance with the previous observations from the XRD measurements and TEM images.

From the previous characterizations, we can conclude that in the case of the iron oxide catalyst, the argon plasma post-treatment does not lead to a full crystallization and phase transformation of the deposited iron oxide sample. Thus, unlike the cobalt oxide layer, the argon plasma post-treatment step cannot be considered as a substitution of the calcination step for the deposited iron oxide layer within the current experimental parameters. A possible assumption may reside in the difference of bond energies between both catalysts. Indeed, a value of 368 kJ/mol for the enthalpy of formation of the Co-O bond was reported versus a value of 409 kJ/mol for the Fe-O bond [313]. The temperature generated at the surface of the sample by ion bombardment during the plasma post-treatment step
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation is not sufficient enough to induce a full phase transformation as the energy required for the formation of a Fe-O bond is higher than the Co-O one.

However, an effect of the plasma post-treatment can be assumed as the pore volume seem has the same order of magnitude than the cobalt oxide catalyst. Therefore, catalytic activity measurements for the deposited iron oxide layer are expected to be low.

4. **Catalytic activity measurements**

4.1 **Results of simple ozonation of PA in batch reactor**

Prior to the catalytic activity measurements of both metallic oxides, the kinetics of the decomposition of ozone in the pyruvic acid solution was assessed in the batch reactor. Samples of initial and final solutions of pyruvic acid after reaction with ozone spaced by 5 minutes were taken during one hour. Degradation of pyruvic acid was calculated using the HPLC technique.

The percentage of degradation was calculated from the HPLC chromatograms with the following equation:

\[
\% \text{ degradation} = \frac{[PA]_0 - [PA]}{[PA]_0} \times 100
\]

- \([PA]_0\) is the initial concentration of pyruvic acid
- \([PA]\) is the concentration of pyruvic acid after treatment

In relationship with the HPLC calibration curve previously established (see Chapter 2), both concentrations were obtained by reporting the value of the calculated area of the pyruvic acid signal in the equation. The reported pyruvic acid concentrations obtained after each treatment correspond to a mean average value for three distinct experiments.

The evolution of the concentration of PA obtained experimentally in the batch reactor is reported in Figure 45.
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Figure n°45: Evolution of the concentration of PA in the batch reactor as a function of time (pH= 3, [PA]₀ = 0.3•10⁻³ mol•L⁻¹, [O₃] = 0.3•10⁻³ mol•L⁻¹) obtained experimentally.

From the previous figure, it can be seen that a final value of 30% ± 4% of degradation was found experimentally after one hour of ozonation with an initial PA concentration of 0.3•10⁻³ mol•L⁻¹ and at pH = 3. The production of ozone being constant, a first-order reaction rate can be considered with the following equation:

\[ C_{PA}(t) = C_{PA}^0 e^{-k_{app} \times t} \]

With: \( k_{app} = kO_3 \times [O_3] \) in s⁻¹

By using reaction rate values from the literature [284] in the same range of concentration for pyruvic acid, i.e., \( kO_3,AP = 1.3•10^{-1} \text{ L•mol}^{-1}•\text{s}^{-1} \) and \( 9.8•10^{-1} \text{ L•mol}^{-1}•\text{s}^{-1} \) respectively at pH = 1 and 7, the corresponding decay values are 13% and 65% after one hour of ozonation.
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Therefore, the experimental value of 30 % obtained for the PA decay is in the same order of magnitude and possibly follows a first order reaction.

4.2 Results of simple ozonation of blank and silica-coated microreactor

Simple ozonation on pyruvic acid was carried out in a blank COC microreactor and in a plasma deposited silica-coated microreactor in order to assess the effect of the COC microchannel and silica layer.

Figure n°46: Simple ozonation performance in blank and silica coated microreactor. Error bars indicate standard deviations for 3 replicate measurements.

As shown in Figure 46, it can be seen that an average value of 30 ± 5% of degradation for simple ozonation of pyruvic acid is reached after one hour in the blank microreactor.

Compared to the previous value of 30 % ± 4 % of degradation in the batch reactor, it can be concluded that the effect of the Teflon tube connecting the batch to the inlet of the microreactor is negligible.

It has to be noted that the change in the initial concentration of pyruvic acid in the stock solution strongly contributes to the reported standard deviation as a value of 0.1 % was found for the standard deviation of HPLC.

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Regarding the results of simple ozonation carried out in the silica-like coated microreactor, it appears that the latter do not exhibit a catalytic activity as the value of 32.9 % ± 2% of degradation is enclosed in the standard deviation of the blank microreactor.

In light of these results, it can be concluded that the blank microreactor and silica coated microreactor do not exhibit a catalytic activity.

4.3 Catalytic ozonation results in iron oxide based catalytic microreactors

4.3.1 Stability of the plasma deposited iron oxide coatings

FAAS measurements were performed after each adsorption and catalytic ozonation tests at the same flow rate, i.e., 3.6 mL$h^{-1}$. Adsorption tests consisted in passing a solution of pyruvic acid ($0.3\times10^{-3}$ mol$L^{-1}$) in the catalytic microreactor during one hour. It has to be noted that washing steps consisting in passing Milli-Q water at a flow rate of 3.6 mL$h^{-1}$ during one hour were performed between each measurement. Results of the FAAS measurements are reported in Figures 47-48.

Results indicate that iron oxide coatings are stable upon adsorption, catalytic ozonation and washing steps as the only detectable amounts were found in the initial washing steps. Values of 0.11 and 0.19 ppm of metallic iron were found respectively for the as deposited and plasma post-treated catalyst after adsorption tests. However, the detected amount of iron in the initial wash solution may find its origin in the leaching of iron oxide nanoparticles of the Fe$_2$O$_3$ superficial layer, inherent to the MO-PECVD process.

In addition, knowing that a value of 60 ppm for 3.6 mL of solution can be calculated if the complete leaching of the deposited Fe$_2$O$_3$ layer is considered, the detected amount of iron in the initial washing step represents less than 0.2 and 0.3 % of the maximum iron amount that can be leached respectively for the as deposited and plasma post-treated iron oxide layer. Therefore, it can be concluded
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation that during the experiments, no leaching of iron from the deposited Fe$_2$O$_3$ layer occurred.

**Figure n°47:** Leaching results for the iron oxide layer deposited by plasma (as deposited and plasma post-treated) after adsorption tests and washing steps.

**Figure n°48:** Leaching results for the iron oxide layer deposited by plasma (as deposited and plasma post-treated) after catalytic ozonation tests and washing steps.

### 4.3.2 Adsorption tests results

Adsorption values for the Fe$_2$O$_3$ catalyst were obtained by passing pyruvic acid in the microchannel at a flow rate of 3.6 mL•h$^{-1}$ during one hour and by determining...
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation.

The final pyruvic acid concentration by the use of HPLC. Between each adsorption test, a washing step was performed as described in section 4.3.1.

**Figure n°49**: Adsorption tests for the iron oxide thin films deposited by plasma (as deposited and plasma post-treated). Error bars indicate standard deviation for 3 replicate catalytic activity measurements for each run.

As shown in Figure 49, the results indicate that the blank microreactor presents here a low adsorption value (4.5 % ± 1%) which probably comes from the increase in the initial surface roughness of the COC top cover during the hot embossing step. Indeed, according to Leech [314], a value of 10 nm was found for the average surface roughness for the COC 6013 grade embossed at 170 °C, i.e., in similar conditions as for our microchannel.

Therefore, the iron oxide based catalytic microreactors do not exhibit a higher pyruvic acid adsorption compared to the blank microreactor.

Moreover, a decrease in the adsorbed pyruvic acid concentration depending on the number of runs can be even observed. At first, this decrease is not significant as the obtained values are enclosed in the standard deviation values of the blank microreactor and could be considered as a reproducibility issue.
Nevertheless, these results could also be possibly explained by a decrease in the number of adsorption sites due to the sustained adsorption of pyruvic acid on the surface of the catalyst. The washing step would be therefore not sufficient enough to remove all the pyruvic acid molecules adsorbed on the catalyst.

4.3.3 Results of catalytic ozonation tests

Figure n°50: Catalytic ozonation performance for the iron oxide layer deposited by plasma (as deposited and plasma post-treated). Error bars indicate standard deviation for 3 replicate catalytic activity measurements for each run.

From the values reported in Figure 50, it can be seen that the Fe$_2$O$_3$ catalyst prepared by MO-PECVD do not present any catalytic activity as, globally, the values are close to the blank (30 ± 5%) and silica-like coated microreactors (33 ± 2%). Although these values are enclosed in the standard deviation of the blank microreactor measurements, they seem to diminish in the same way than the adsorption tests results. Therefore, it can be concluded that the deposited Fe$_2$O$_3$ layer do not present a catalytic activity and that the obtained values are due to poor reproducibility.
The absence of catalytic activity could reside in the fact that the plasma post-treatment step does not manage to achieve an adequate crystallization in comparison to the deposited cobalt oxide layer, leading to a nonexistent catalytic activity as previously expected from the characterization results of the iron oxide layer.

Indeed, Rubashov et al. [315] studied Fe$_2$O$_3$ as a potential catalyst for the decomposition of ozone. The catalytic activity of Fe$_2$O$_3$ was reported to be nonexistent when the catalyst was in the form of aggregated particles whereas when it was in the form of dispersed particles, the catalyst was shown to be efficient for the decomposition of ozone. Moreover, the stability of Fe$_2$O$_3$ was relatively low and the formation of oxygen directly associated with the surface led to the poisoning of the catalyst in the manner of a Mars-Van Krevelen mechanism due to lattice oxygen [316]. Given the previous characterization results, we can conclude that the plasma post-treatment conditions used here lead to a non-efficient catalyst in ozonation of pyruvic acid.

4.4 Catalytic ozonation results in cobalt oxide based catalytic microreactors

4.4.1 Stability of the plasma deposited cobalt oxide coatings

In the same way than the iron oxide catalyst, leaching of the deposited Co$_3$O$_4$ layer was assessed after performing adsorption and ozonation of PA using FAAS measurements.
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As shown in Figures 51-52, both prepared cobalt oxides present a strong stability towards adsorption and catalytic ozonation tests as well as towards washing steps, as only the initial washing step present a sufficient amount of cobalt that can be detected by FAAS measurements just like in the case of the iron oxide catalyst.
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In a similar way, by considering a full leaching of the cobalt oxide layer, a value of 97 ppm can be calculated in 3.6 mL of solution. Thus, the leaching measured after the initial washing step only represents 0.59 % and 0.3 % of the total catalyst layer, respectively for the as-deposited cobalt oxide layer and plasma post-treated sample. Therefore, it can be concluded that the plasma deposited cobalt oxides are also stable upon adsorption and catalytic ozonation tests.

4.4.2 Adsorption tests results

**Figure n°53:** Adsorption tests for cobalt oxide thin films deposited by plasma (as deposited and plasma post-treated). Error bars indicate standard deviations for 3 replicate catalytic activity measurements for each case.

As shown in Figure 53, the adsorption values of PA on the surface of both cobalt oxides is close to the blank microreactor one as previously found for the iron oxide layer.

The works of Gumuchian [317] showed an adsorption value of 33 % using 3 g of a commercial Co₃O₄ powder (measured specific surface area of 11.8 m²/g) with a
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starting PA concentration of 5 mmol·L⁻¹ for a S/Q ratio of 200 000 m²/mol; S/Q given by the following equation:

\[
\frac{S}{Q} = \frac{m_{catalyst} \times S_{BET}}{[PA] \times V_{solution}}
\]

In the present study, the S/Q ratio was determined to be equal to 12 000 and 14 000 m²/mol respectively for the as-deposited cobalt oxide and plasma post-treated cobalt oxide layer. Based on the Langmuir isotherm established by Gumuchian for cobalt oxide, it can be concluded that the reported values of 4.6 % and 3.7% are relevant as the S/Q here is 10 orders of magnitude lower.

Once again, a decrease in the adsorbed pyruvic acid concentration depending on the number of runs can be even observed and could be considered as a reproducibility issue.

Nevertheless, these results could also be possibly explained by a decrease in the number of adsorption sites due to the sustained adsorption of pyruvic acid on the surface of the catalyst. The washing step would be therefore not sufficient enough to remove all the pyruvic acid molecules adsorbed on the catalyst.

4.4.3 Determination of the concentration of active sites for the Co₃O₄ catalyst

Based on the previous BET measurements of the plasma post-treated cobalt oxide layer, the concentration of active sites of the catalyst can be determined by a simple ratio between the amount of adsorbed pyruvic acid and the determined real surface area of the catalyst:

\[
C_s = \frac{n_{adsorbed pyruvic acid}}{S}
\]

Indeed, with the simple adsorption tests which consisted in passing pyruvic acid in the catalytic microreactor, a value of 3.7% ± 0.3% of adsorbed pyruvic acid was determined by HPLC measurements.
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Consequently, with an initial concentration of pyruvic acid of 0.3 mol•L\(^{-1}\) and a flow of 3.6 mL•h\(^{-1}\), the total amount of adsorbed pyruvic acid after one hour corresponds to a value of 5•10\(^{-8}\) mol.

From the BET measurements of the plasma post-treated layer, a value of 3•10\(^{-2}\) m\(^{2}\) was found for the total developed surface area. Therefore, with the previous equation, a value of 1.8•10\(^{-6}\) mol/m\(^{2}\) was found for the concentration of actives sites. Moreover, in her thesis, Gumuchian found a similar value (1.9•10\(^{-6}\) mol/m\(^{2}\)) using commercial Co\(_{3}\)O\(_{4}\) in the form of nanoparticles (500 nm of diameter) which could lead to the assumption that the adsorption of pyruvic acid do not depend of the morphological structure. However, this assumption will not be further developed here.

In addition, a simple calculation can be done in order to evaluate the steric hindrance induced by pyruvic acid on the surface of the catalyst by using density functional theory (DFT) model evaluation and more specifically the total polar surface area (TPSA). Indeed, TPSA is a computer based simulation that takes into account the polar surface of a molecule. In our case, the pyruvic acid molecule is assumed to be adsorbed on the surface of the catalyst via the polar functions. A value of 3•10\(^{-6}\) mol/m\(^{2}\) was found considering a polar surface of 54•10\(^{-19}\) m\(^{2}\) with the TPSA measurements.

These results indicate that at saturation, the quantity of pyruvic acid adsorbed on the catalyst surface is the maximum possible due to steric hindrance.

Regarding the equilibrium constant K\(_{A}\), between the adsorption/desorption rate of PA on the surface of the catalyst, the latter was determined by the reporting the initial concentration of PA (0.3 mol/m\(^{3}\)) on the Langmuir isotherm obtained by Gumuchian and a value of K\(_{A}\) = 2 mg/g was found.

4.4.4 Results of catalytic ozonation tests
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Figure n°54: Catalytic ozonation performance for cobalt oxide thin film deposited by plasma (as deposited and plasma post-treated). Error bars indicate standard deviations for 3 replicate catalytic activity measurements for each case.

As shown in Figure 54, it can be seen that the cobalt based catalysts prepared by MO-PECVD present a higher catalytic activity than the iron oxide based one. Moreover, the effect of the plasma post-treatment can be clearly observed as the microreactor with the plasma post-treated catalytic layer exhibits a higher activity (71 ± 1%) compared to the initial cobalt oxide layer (47.6 ± 1%). Actually, the decay of the pyruvic acid concentration due to catalysis adds an additional 40 % ± 6% of degradation as measurements performed in the initial blank microreactor showed a value of 30.7 ± 5%.

Unfortunately, for both Co₃O₄ microreactors, a decrease in the catalytic activity can be noticed despite the intermediate washing steps. However, a final washing step consisting in sending a solution of Milli-Q water with dissolved ozone (0.3 mM) during one hour at a flow rate of 3.6 mL•h⁻¹ in the catalytic microreactor lead to a regeneration of the catalyst. In other words, a re-use of the catalytic
Chapter 4: Development of catalytic microreactors: comparison of the performance of plasma-deposited iron and cobalt oxides in catalytic ozonation microreactor is possible as the decrease of catalytic activity is not an irreversible phenomenon.

In order to understand the decrease in the catalytic activity of the cobalt oxides, a first assumption regarding an eventual poisoning of the catalyst can be made, as no leaching of the deposited layer was found by FAAS measurements.

This assumption in regards to the deactivation of the cobalt oxide catalyst may reside in the decrease of number of actives sites due to adsorption of oxidation products produced during ozonation of pyruvic acid. From the literature [318], by-products of the ozonation of pyruvic acid may be identified as acetic acid and oxalic acid. Thus, due to blocking of the active sites, these adsorbed products would lead to a poisoning effect preventing new flowing pyruvic molecules to access the catalyst actives sites and further be decomposed upon reaction with ozone. A possible explanation of the regeneration step can be explained by the fact that the dissolved ozone molecules will react with the adsorbed species. Thus, reaction of the latter with ozone would lead to the cleaning of the active sites of the Co$_3$O$_4$ catalyst. The latter assumption implies that ozone reacts preferentially with pyruvic acid to the detriment of the adsorbed oxidation products.

The comparison of the reactivity of pyruvic acid and its oxidation products with ozone supports this assumption. Indeed, the reaction rate constants of direct ozonation are $3\times10^{-5}$ and $4\times10^{-2}$ L•mol$^{-1}$•s$^{-1}$ respectively for acetic acid and oxalic acid [319] whereas a reaction rate constant of $3.3\times10^{-1}$ L•mol$^{-1}$•s$^{-1}$ was experimentally determined for pyruvic acid.

Another assumption regarding the deactivation of the catalyst may be due to the change in the oxidation state of the active sites during the different runs. This assumption may be addressed as a Mars-van Krevelen mechanism type where the intermediate species originating from the ozone self-decomposition poison the catalyst.
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Assuming that the degradation of pyruvic acid is essentially due to heterogeneous catalysis, the catalytic activity will be related to the exposed facets of the cobalt oxide nanoparticles. The cobalt oxide obtained here is of the Co$_3$O$_4$ spinel-type consisting in octahedrally coordinated Co$^{3+}$ and tetrahedrally coordinated Co$^{2+}$ [320].

The [110] plane of Co$_3$O$_4$ has been reported to be the most catalytically active one as it favors Co$^{3+}$ sites [321,322]. Indeed, this assumption was validated recently by calculating the surfaces energies of an ideal cobalt oxide crystal based on the density function theory (DFT) [323]. Su et al. demonstrated that the [111] plane provides more active Co$^{3+}$ sites. Nevertheless, the [110] plane of the Co$_3$O$_4$ spinel-type nanoparticle plane has the lowest surface energy, thus suggesting the most stable facet. Based on the previous XRD measurements and in accordance with the results from the literature, we can hypothetically presume that the [110] plane is responsible for the catalytic activity.

Therefore, the deactivation of the catalyst can possibly be explained by the considering the intermediates species generated during the self-decomposition of ozone. As an example, different species such as O$_2$$^{2-}$ and O$_2$$^•$- [324] with respective standard reduction potentials of -2.8V and -0.66V [325] may play the role of reducing agents.

Considering the O$_2$$^•$- specie, reduction of the cobalt oxide can be written as:

$$O_2^{-} + Co^{3+} \rightarrow O_2 + Co^{2+}$$

Derived from the Nernst equation, the equilibrium constant can be calculated as follows:

$$\log K = \frac{(E^0_{Co^{3+},Co^{2+}}) - (E^0_{O_2,O_2^{-}})}{0.059}$$

A value of 7.3•10$^{41}$ was found indicating that this reaction is strongly promoted. Assuming this specie comes from the following self-decomposition of ozone [326], generation of the oxygen superoxide specie can be written as follows:
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\[ O_3 + OH^- \rightarrow O_2^- + HO_2^* \]

According to the works of Rao et al. [327] in an aqueous solutions, reduction of the \( O_2^- \) specie was found to be not reversible in equilibrium conditions.

The regeneration can further be explained by considering the standard reduction potentials of \( E^0 (Co^{3+}/Co^{2+}) = 1.81 \) V and \( E^0 (O_3/O_2) = 2.07 \) V with the following equation:

\[ 2O_3 + Co^{2+} \rightarrow 3O_2 + Co^{3+} \]

Like previously, the equilibrium constant can be calculated as follows:

\[
\log K = \frac{2 \times ((E^0 O_3, O_2) - (E^0 Co^{3+}, Co^{2+}))}{0.059}
\]

A value of \( 6.5 \times 10^8 \) was found for the previous equilibrium constant indicating that this reaction is less promoted than the reaction between oxygen superoxide and the catalyst in pure ozonation.

In addition, assuming that ozone reacts in an equimolar ratio of 1 with PA, this regeneration step requires 2 times more ozone than in the catalytic ozonation step, indicating a possible decrease in the availability of ozone molecules to effectively regenerate the surface during the catalytic ozonation step.

However, the reaction between ozone and the oxygen superoxide must also be considered:

\[ O_3 + OH^- \rightarrow O_2^- + HO_2^* \]

With \( k = 70 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \) from [326]

\[ O_3 + O_2^- \rightarrow O_3 + O_2 \]

With \( k = 9 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \) from [328]
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Therefore, from these rate constant values, it can be seen that ozone can oxidize the Co$^{2+}$ present on the surface to Co$^{3+}$ as the reaction between ozone and the superoxide specie is more rapid than the generation of this latter, leading to a regeneration of the catalytic layer.

In the light of these results and assuming that the reaction between the superoxide specie and PA is favored, it can be concluded that the previous formulated assumption (deactivation of the layer is assumed to be due to the reaction of the oxygen superoxide with the cobalt oxide layer) during the catalytic ozonation tests is probably wrong.

Unfortunately, to the best of our knowledge no values were found in the literature for the reaction rate constant for the latter reaction. Therefore, the most probable hypothesis for the deactivation of the layer resides in the fact that acetic acid and oxalic acid are adsorbed as by-products resulting from the catalytic ozonation of pyruvic acid on the surface of the cobalt oxide catalyst.

5. Conclusion

A MO-PECVD plasma process was used to elaborate catalytic microreactors by depositing and activating iron and oxide-based catalysts at low temperatures. Characterization results showed that the plasma post-treatment step successfully induced a phase transition change and a structural refinement of the surface of the initial deposited layer.

The efficiency of both catalysts was assessed in a catalytic ozonation process with pyruvic acid as a refractory probe compound. In the case of iron oxide layer, HPLC measurements demonstrated the inactivity of such catalyst even for the plasma post-treated sample. One assumption resides in the conditions used for the plasma post-treatment that are not fully optimized for the iron oxide layer in order to successfully achieve an adequate crystallization. In comparison to the deposited cobalt oxide layer, the decomposition rate of an organic pollutant with ozone was increased in the presence of a cobalt oxide layer.
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In presence of the plasma deposited cobalt oxide layer, 20 % of additional degradation was found whereas when the layer was post-treated by argon plasma, the effect was doubled (40%), indicating a synergistic effect between the surface morphology of the coating and PA.

These results are very promising considering the low residence time of only 0.75 second in the microreactor. Moreover, the use of plasma processes for the deposition catalyst offers interesting perspectives in the depollution field as it minimizes the potential nanotoxicity of the surface and suggests a long-term viability of the coating as demonstrated with FAAS measurements.

However, a decrease of the catalytic activity for the post-treated cobalt oxide layer was found indicating a possible coverage of the active sites by intermediate products generated during catalytic ozonation. Nevertheless, the catalyst was regenerated by passing ozone dissolved in Milli-Q water indicating that this phenomenon is reversible. Therefore, deactivation could possibly be avoided by increasing the \( \text{O}_3/\text{PA} \) ratio.

Further investigations regarding the kinetics of catalytic heterogeneous ozonation will be studied in the next chapter by performing computer simulations using the Comsol Multiphysics software.