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Soot oxidation activity of doped ceria. Influence of dopants

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ABSTRACT

Catalytic conversion of carbon monoxide (CO) and nitrogen oxides (NO_x) has been studied due to its importance for reducing hazardous emissions of vehicles to the environment.^[1] Typically, the exhaust gases from automobiles are purified by a three-way catalyst (TWC) which aims at the simultaneous treatment of carbon monoxide, hydrocarbons and nitrogen oxides.^{[2], [3]}

Soot particles are released from diesel engine exhausts and they are dangerous for the environment and health. These particles can cause several problems like allergic, respiratory and cardiovascular diseases. At the moment there are several solutions for this problem, but most of them need periodic regeneration to avoid the filters being blocked by the soot. However, the best solution is controlling this emissions by catalytic conversion of the particles to harmless CO₂ and H₂O.

Designing advanced doped ceria (CeO₂) materials has extensive uses in several environmental, energy and industrial catalytic applications. CeO₂ has a significant oxygen storage capacity (OSC), relative ease of oxygen vacancy formation and a great facility to switch between the oxidation states of the cerium ion (Ce³⁺/Ce⁴⁺).^[2]

The aim of this project has been to study different series of doped ceria catalysts with different synthetic methods towards environmental applications like soot oxidation catalysis. Various transition metals of varying size and reducibility namely, copper (Cu), iron (Fe) and manganese (Mn) have been selected as dopants. Different preparation methods for the synthesis of ceria-based nanomaterials have been employed: co-precipitation^{[7], [8]}, hydrothermal synthesis^{[9][16]}, wet impregnation and flame spray pyrolysis (FSP).^[4]

In our study, we focus more in two specific preparation methods, coprecipitation and hydrothermal synthesis rather than FSP or wet impregnation to incorporate the dopants into ceria lattice because they are a scalable and promising technique for this type of reactions.

The formation of homogeneous solid solutions and their respective physicochemical properties have been confirmed by employing XRD analysis and BET surface area measurements. Moreover, the physicochemical properties of the doped ceria materials have been comparatively analyzed to correlate the influence of dopants with their improved behavior in soot oxidation reaction.

The reaction we used for evaluating the catalysts, soot oxidation, was carried out in air flow using a thermogravimetric analyzer (TGA) from room temperature to 900°C by increasing the temperature with a constant heating rate.. This technique provided us with data about the standard oxidation temperature of soot without a catalyst, and the extent of the decrease of the oxidation temperature when a catalyst is added. We used this technique in order to compare the results of the different preparation methods with different metals as a dopants. Experimental results point out that the FSP made catalyst with a higher (BET) surface area and smaller particles is able to oxidize soot particles at a much lower temperature. Also the hydrothermal synthesis made catalysts are able to oxidize soot even with lower (BET) surface area and bigger particles than FSP. However, co-precipitation catalysts did not manage to significantly lower the oxidation temperature of soot and this makes it a poorly performing catalyst.^[10]

1. OBJECTIVES

The following project introduces the main different objectives:

- Study the performance of CeO_2 catalyst with different transition metals of varying size and reducibility like copper (Cu), iron (Fe) and manganese (Mn) as dopants.

We used those transition metals with a molar ratio of 5wt% or 10wt%.

- Study the influence of our catalysts with different transition metals as a dopants using different synthetic methods such as co-precipitation, hydrothermal synthesis, wet impregnation and flame spray pyrolysis (FSP).

Depending on which the synthetic method has been used for synthesizing the catalyst we will obtain very different results for the particle size, (BET) surface area and also in soot oxidation reaction performed in a thermo gravimetric analyzer.

- Study of the catalytic activity in the soot oxidation reaction.
- Study of precision and reproducibility of the method for the soot oxidation reaction.

The methods used for testing the catalysts were validated by carefully choosing the ratio of catalyst and soot.

2. INTRODUCTION

Nowadays, catalysts are the workhorses of technologies for chemical and material synthesis such as fuel production and they are great promoters of environmental solutions.^[1] As it is known, there are a lot of serious pollution problems, like the massive waste of side products most of which are very dangerous for the nature. Catalysts can help solve this serious problem in industry being active and selective and helping main reactions in becoming greener.^{[6]. [12]}

Heterogeneous catalysis always occurs on the surface of a solid catalyst, whose composition and surface geometry will determine its catalytic properties. Moreover, the electronic surface of a solid particle is determined by the size and composition. However, talking in macroscopically terms its catalytic properties can suffer changes depending on its composition, size and morphology.^{[6]. [12]}

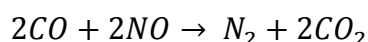
Cerium is one of the most abundant and rare earth metal, where the main sources of cerium are the light rare earth element minerals such as allanite, monazite and others. Its oxide (CeO_2) has been investigated in this heterogeneous field because it has been found to give the highest conversion of environmental pollutants^[2] – due to its remarkable capacity to store and release O_2 through the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple.^[2] Because of these redox properties, CeO_2 is used in a wide range of applications.^[6]

This capacity to store and release O_2 through the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple makes much easier to integrate the metal inside the vacancies on the crystal.^[2] The oxygen storage capacity takes place in both, at the surface and in the bulk for the obtained CeO_2 . Moreover, it can be used in this field as a catalyst and as a support for noble metals. This feature can easily be enhanced with the addition of the transition metals such as manganese, iron or copper. Noble metals have also been used as a dopant to improve its activity, selectivity and even for improving its thermal stability.^[12]

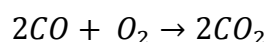
The main application for doped ceria (CeO_2) is to be used as a promoter for the three-way-catalyst (TWC) which aims at the simultaneous treatment of carbon monoxide, hydrocarbons and nitrogen oxides in petrol engines.^[5]

These three reactions have been studied for reducing hazardous emissions to the environment:

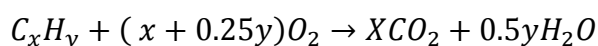
- The reduction of nitrogen oxides



- Oxidation of carbon monoxide



- Oxidation of hydrocarbons



There are other pollutants emitted from the diesel engine exhaust like the soot particles. These particles are very dangerous for health and environment where most of the health problems are related to respiratory problems. At the moment there are some solutions for this problem, but they are not definitive because most of them need periodic regeneration to avoid the filters being blocked by the soot.

We aim at an alternative approach, in which the doped ceria is able to oxidize the soot, allowing us to control the diesel particulate emissions by catalytic conversion of these particles to non-toxic CO_2 and H_2O .^[2]

In this project we synthesized different catalysts with different procedures and metals as a dopants to study the best catalyst being able to oxidize the soot at the lowest temperature. The different transition metals of varying size and reducibility that were studied are copper (Cu), iron (Fe) and manganese (Mn). The different preparation methods for the synthesis of ceria-based nanomaterials have been employed are co-precipitation, hydrothermal synthesis, wet impregnation and flame spray pyrolysis (FSP). Each method will be explained in Chapter 3 for a better understanding and in the experimental part all the necessary steps for synthesizes this catalyst will be explained in detail.

3. - CATALYST SYNTHESIS

For preparing our catalysts different methods were used like flame spray pyrolysis (FSP), co-precipitation, wet impregnation and hydrothermal synthesis.

In this chapter each method will be explained, followed by a step-by-step explanation on how the catalysts were prepared.

3.1. Flame spray pyrolysis synthesis (FSP)

The method consists in a gas phase exothermic combustion synthesis where the catalyst's production can include a big range of materials in the nanostructured powders form with thermal stability, high specific surface area and particle size in the range of a few nanometers. The FSP technique can control the degree of aggregation and agglomeration also the porosity and the crystallite size and phase by changing flame conditions^[4] It can also closely control nanoparticles by precursors, solvents and other instrumental parameters. Moreover with this technique the nanoparticles are typically fully oxidized and crystalline.^[13]

FSP has many characteristics but the most important are the following ones. The short process chain, the flexibility of the process, the production of multi-component materials in one step, the possibility of process scale-up for cost-efficient large scale-production of nanoparticles. That is because in each process we can modify the parameters and the quantity of metalorganic compounds dissolved in the liquid phase.^{[6]. [12]}

Moreover, the catalysts are produce by FSP have a high production rate, a high temperature resistance and a high surface area.^[13]

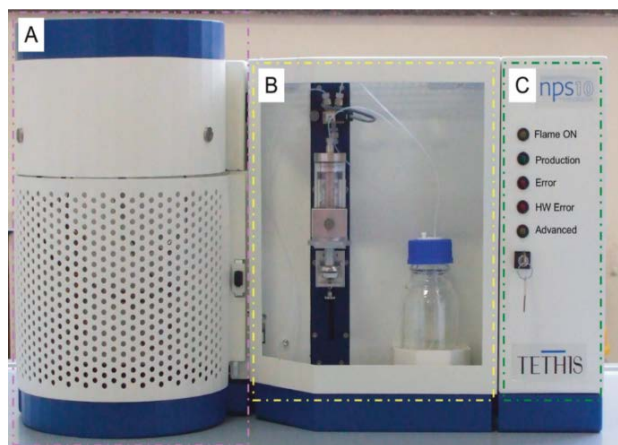


Figure 1: Experimental setup for FSP. (NPS-10, TethisLab)

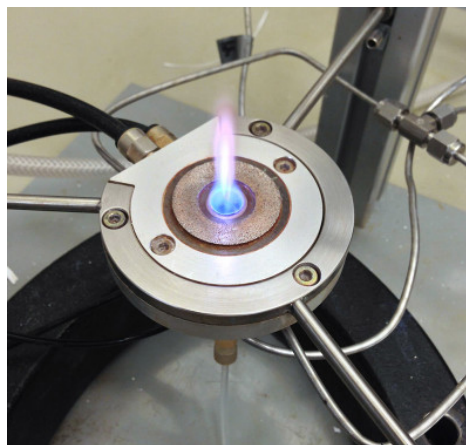


Figure 2: FSP burner in the nozzle unit.

The setup has three parts: the nozzle unit (A), the dispersing system (B) and the control unit (C) as it is shown in **Figure 1**. **Figure 2** shows the burner inside the nozzle unit (A) where the exothermic combustion of a spray of a liquid phase mixture containing metalorganic compound and a solvent is dispersed (B) into a flame where the resulting mixture droplets are combusted generating small clusters, which grow up by collisions and sintering processes taking place in the high temperature environment of the flame. Nevertheless, the growth process can be controlled modifying the precursor concentration and the flame parameters.

There's an additional oxygen flow that provides the complete combustion of the solvent and the metallorganic compound in water and CO_2 . Moreover, the rapid quenching and short residence time of the spray flame prevents noble metals from serious sintering thereby maintains high noble metal dispersion on the surface of the supports. [6]. [12]

3.1.1. Support materials and catalyst preparation

For starting step by step with the procedure of the synthesis, first of all in the computer we have to open the program called NCS and open the methane and oxygen flows. The program will let us change all the parameters we want: flow of methane and oxygen gases, injection speed, and pressure.

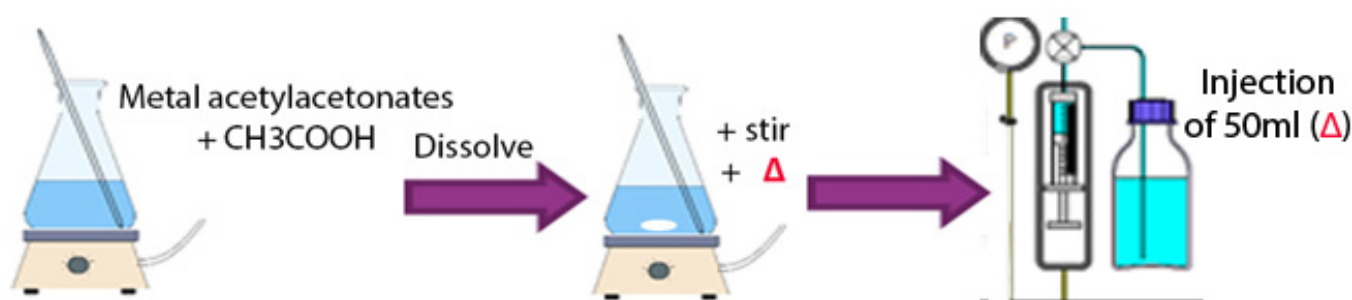


Figure 3: First and second step of the procedure of the synthesis. Preparation of the 150ml solution with ceria acetylacetonate, glacial acetic acid and the dopant acetylacetonate and the injection of 50ml of the solution.

For the pure CeO_2 , the precursor solution of 150ml was prepared by dissolving appropriate amounts of cerium (III) acetylacetonate ($\text{Ce}(\text{acac})_3 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich) in glacial acetic acid (Sigma-Aldrich, purity 99.7%) while stirring vigorously at 80°C , as **Figure 3** shows. The metal concentration was kept constant at 0.1 M. Heat is needed to solubilize the solution otherwise it will not be homogeneous.

Pure ceria was synthesized using the flame spray pyrolysis (FSP) technique. The experimental apparatus of FSP is described by Mädler et al.^[15] **Figure. 2** shows the burner inside the nozzle unit. It consists of a nozzle for the dispersion of liquids, a premixed flamelet ring for ignition and stabilization of the liquid spray and an annular sintered metal port for optional introduction of an additional oxygen flow to influence the environment of the flame.

In our experiments, as shown in **Figure 3** and **Figure 4** the precursor solution was fed into the center of a methane/oxygen flame by a 50 mL syringe at a rate of 5 mL/min. This is an important step where we have to be careful and pay attention to the solution because after a while it is no longer at 80°C and starts to precipitate and the FSP can have huge blocks afterwards.

The premixed methane/oxygen gas was kept constant with a methane flow of 1.5 L/min and an oxygen flow of 3 L/min to maintain the supporting flame. At the nozzle, the solution was dispersed into a fine spray by a 5 L/min O_2 flow and subsequently ignited by the flame. Thereby nanoparticles are formed by nucleation from the gas phase and subsequent particle growth. The pressure drop at the capillary tip was kept constant at 2 bar. The freshly-produced were collected by a suitable filtering system made of glass microfibre filter (Albet) with the aid of a vacuum pump (Busch) place above the flame without any type of post-treatment steps. The nanoparticles are ready to use. The schematic diagram of the overall FSP process is shown in **Figure 4**.

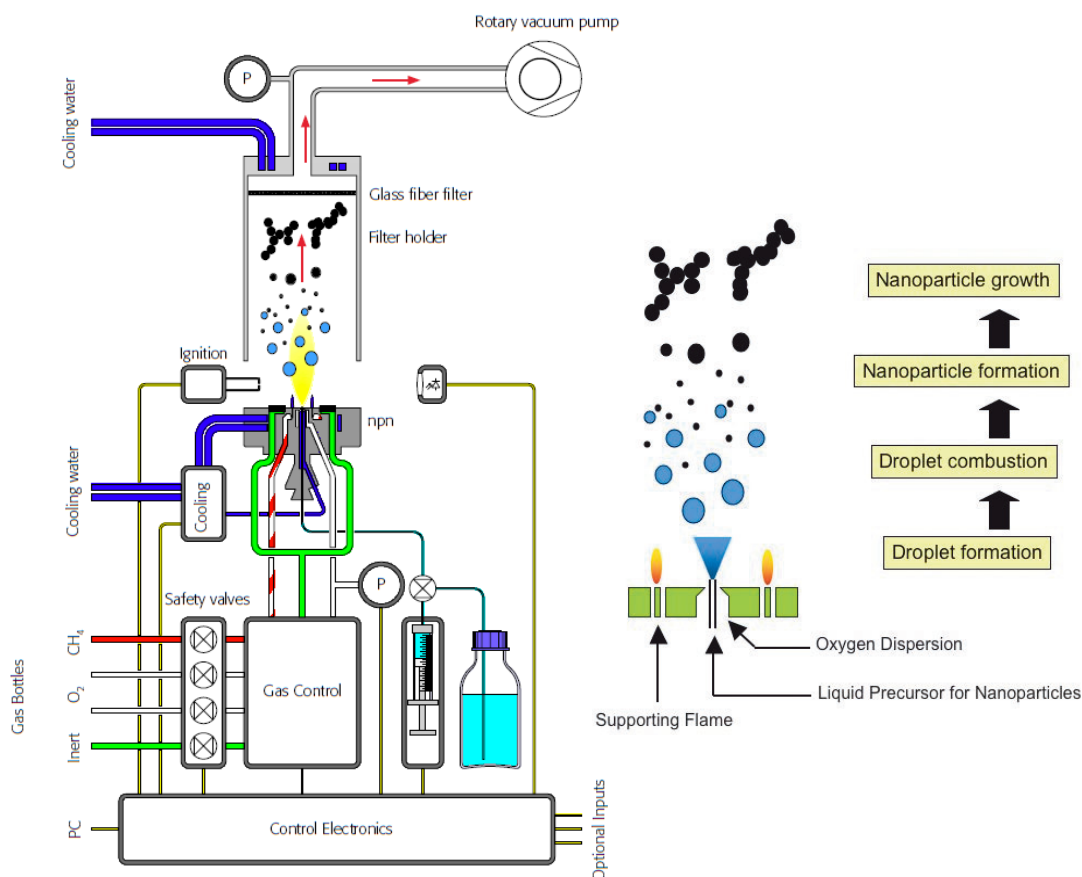


Figure 4: Schematic representations of FSP process.

This technique also offers the possibility of the production of multi-component materials in one step. For this experiment only manganese (Mn) as dopant for the support material (CeO_2) was chosen for lack of time but also other metals such as iron (Fe) or copper (Cu) can be tested.

The catalyst with manganese was directly synthesized by FSP technique with different metal loadings. Those catalysts were prepared by dissolving appropriate amounts of cerium (III) acetylacetonate ($\text{Ce}(\text{acac})_3 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich) and manganese (II) acetylacetonate ($\text{Mn}(\text{acac})_2$, Sigma-Aldrich) in glacial acetic acid (Sigma-Aldrich, purity 99.7%) while stirring vigorously at 80°C as the **Figure 4** shows. Also in this case, heat is important and needed to solubilize perfectly everything and keep the solution homogeneous because more than one metal have been used for preparing the solution.

The metal concentration was kept constant at 0.1 M and the mole fraction of the dopant was 2.5% or 10% for 150ml of the prepared solution.

For this experiment the procedure is the same as before. As shown in **Figure 3** and **Figure 4** the precursor solution with manganese as dopant was fed into the center of a methane/oxygen flame by a 50 mL syringe at a rate of 5 mL/min. Where the premixed flow gas was kept constant with an oxygen flow of 3L/min and the methane flow of 1.5L/min. Once the solution arrives at the nozzle, a dispersion of the liquids occurs and a premixed flamelet ring for ignition and stabilization of the liquid spray an annular sintered metal port for option introduction of an additional oxygen flow to influence the environment of the flame.

Finally, nanoparticles are formed by nucleation from the gas phase and the catalyst was collected by a suitable filtering system made of glass microfibre filter (Albet) with the help of the aid of a vacuum pump (Busch) placed above the flame without any type of post-treatment steps. The nanoparticles are ready to use.

This technique can be further studied using a two-steps synthesis, synthesizing pure ceria (CeO_2) with a posterior wet-impregnation of the catalyst with manganese (Mn), iron (Fe) or copper (Cu) as dopants and with different metal loadings. Dissolving the catalyst and the dopant in 10ml of water and stirring for 30min at room temperature. Afterwards, heating the hot plate at 110°C until they were completely dry. Once without water, the impregnated support was dried for 30min in the catalyst oven and finally they were calcined in the calcination oven for 4h in air at 300°C in an 80/20 He/O_2 flow at ambient pressure for 3h.

Pitifully, for lack of time this part of the project could not finish.

For the sake of simplicity, the samples synthesized with the flame spray pyrolysis (FSP) method will be defined as FSP, followed by a number identifying the dopant percentage in the sample and the symbol of the dopant. For instance, FSP_1Mn is a CeO_2 sample prepared with flame spray pyrolysis synthesis, doped with 1% molar Mn.

3.2. Hydrothermal synthesis

This method of synthesis is very useful because it allows several methods of crystallizing products from high temperature aqueous solutions at high pressure under different NaOH concentrations using $\text{Ce}(\text{NO}_3)_3$ as the cerium source. It can also be defined as a synthesis method to obtain pure oxides depending on the solubility of minerals in hot water under high pressure.^[16] The crystal growth is performed inside a steel pressure vessel called autoclave as **Figure 5** shows.



Figure 5: Picture of a steel pressure vessel used for the hydrothermal synthesis.

However hydrothermal synthesis not only offers one possibility of synthesis of oxides of different crystal shape and size. This method offers different possibilities of shape-selective synthesis of inorganic materials where is important scientifically and technologically due to their unique shape-dependent material

properties.^[16] Furthermore this method is one of the most effective and economical routes because of the temperature synthesis we chose, its composition and morphological control and powder reactivity. So, depending on the temperature of the oven and if the autoclaves are being rotated or not, we will obtain a different crystal shape and size.^[17] These different crystal shape can be single-crystalline and uniform nanopolyhedra, nanorods, and nanocubes of cubic CeO_2 . It has been demonstrated that during the synthesis the product can be found in an intermediate hydroxyl species and transform into CeO_2 due to the elevated temperature, together with a high concentration of base. Those are the main factors responsible for the shape evolution of the crystal.^[16]

The most commonly used procedures for hydrothermal synthesis for our experiments are two as the **Figure 6** shows: without rotation at 100°C to obtain nanorods and with rotation at 180°C to obtain nanocubes.^[18]

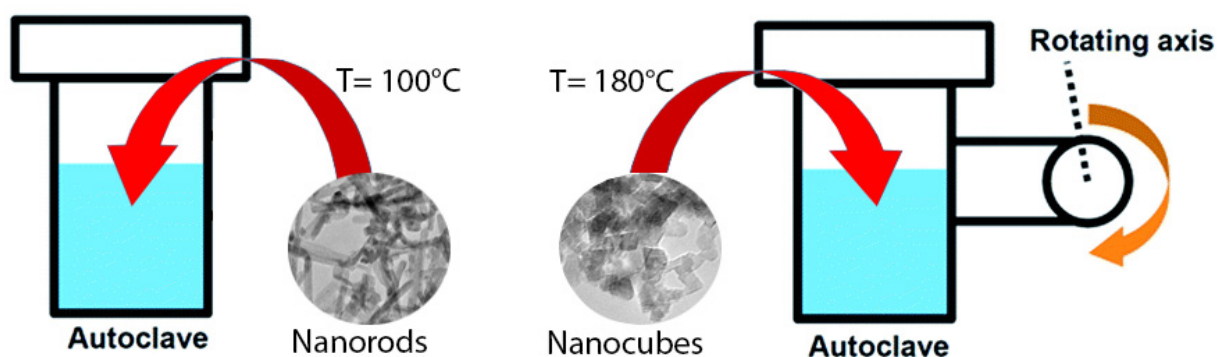


Figure 6: Two different procedures for hydrothermal synthesis of how to obtain specific crystal shape. The left autoclave shows how to make nanorods and the right one show how to make nanocubes.

Although, there are two procedures that we use the most, in this project we decided to aim for the production of transition metal-doped CeO_2 nanorods instead of nanocubes. Nanorods have proved to have a higher oxygen storage capacity (OSC). The oxygen storage capacity takes place at the surface, however some measurements performed at 400°C revealed that not only takes place at the surface, also takes place in the bulk for the obtained CeO_2 nanorods and nanocubes.^[6] Moreover this feature can be enhanced with the addition of the transition metals such as manganese (Mn), iron (Fe) or copper (Cu).

So, for the synthesis of nanorods the crystal growth is performed inside a steel pressure called autoclave at 100°C without rotation for 24h.

3.2.1. Catalyst preparation

For preparing the catalyst a base and the metal precursors are needed. As a base, we chose to use NaOH , in order to be able to increase the pH easily. The precursor that has been used is $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, purity 99%) where the mole fraction of Ce was 95% or 90%, and the mole fraction of the dopant was 5% or 10% respectively. For this experiment the metals as dopant we chose were different transition metals of varying size and reducibility such as copper ($\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich)), iron ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich)) and manganese (II) ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich)).

For that process we have some main steps:

Reaction step

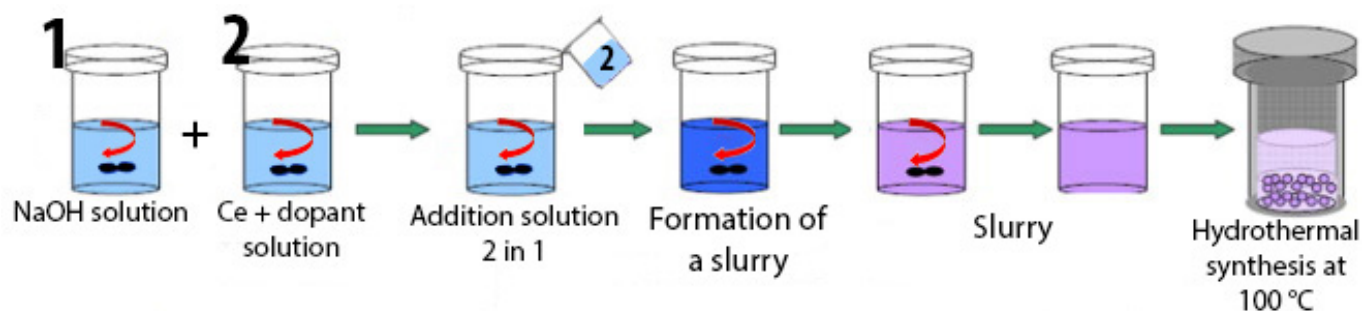


Figure 7: Reaction steps for hydrothermal synthesis.

24 g of base were weighted and dissolved in deionized water in a beaker under vigorous stirring. It's a very exothermic reaction, and it is needed to wait until the solution is at room temperature for the following step. In another beaker, the ceria precursor with the dopant precursor were mixed and solubilized taking care of the weight of each for getting a 95% or 90% weight of the ceria precursor, and a 5% or 10% of the mole fraction of the dopant.

Once the base is at room temperature, the solution from the precursor's beaker was poured into the base's beaker and was stirred for 2h. Immediately the product starts to appear as a precipitate and that's what it's called formation of a slurry. After 2h we have all the slurry. Depending on the dopant, the color of the slurry will be different: brown for manganese, red for iron and green for copper.

Afterwards, the slurry was poured inside a Teflon liner with more deionized water, taking care of filling only the 80% of the capacity. The Teflon liner was located inside the autoclave and put inside an oven at 100 °C for 24h without rotation. The rotation would favor the formation of nanocubes instead of nanorods.

Washing + dry step

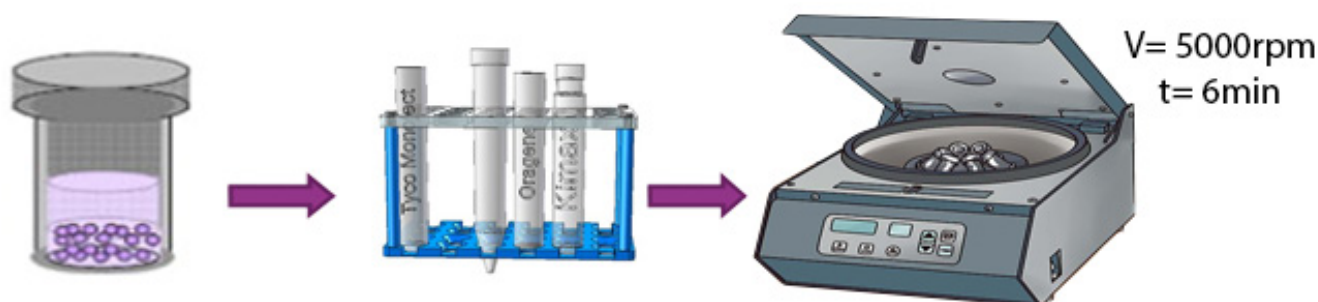


Figure 8: Steps for washing the catalyst using a centrifuge.

As **Figure 8** shows, a centrifuge was used for washing our samples three times with deionized water to eliminate the anionic impurities for 6min and 5000rpm each time. Then, the samples were washed with ethanol two or three times more

For better drying, a vacuum oven was used for 1h at 70°C.

Calcination step

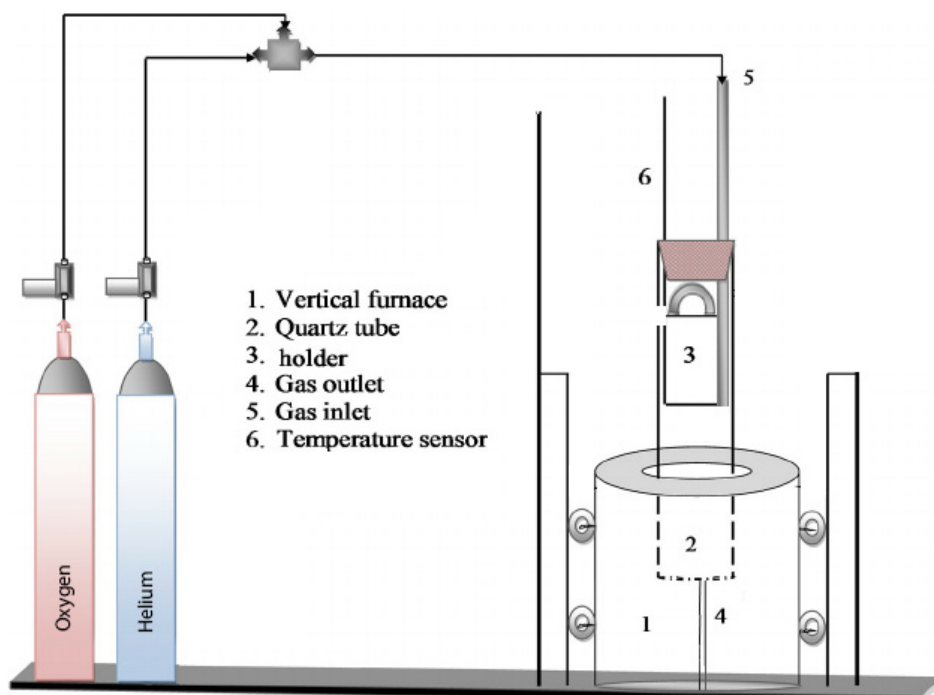


Figure 9: Esqueme of a calcination oven.

Once the catalyst were dry, they were calcined in a calcination oven. Calcination is the process of subjecting a catalyst to a temperature ramp, while being in contact with an oxidizing atmosphere (static or in flow).

The process of calcination is usually meant to drive off carbon dioxide (CO₂) or other volatile constituent and impurities, to oxidize a part of or the whole substance and to drive off water that can be present as adsorbed moisture, as can be water of crystallization.

For this calcination process the catalysts were inside the oven for 4h at 500°C in an 80/20 He/O₂ flow at ambient pressure as **Figure 9** shows.

For the sake of simplicity, the samples synthesized with the hydrothermal synthesis method will be defined as Rods, followed by a number identifying the dopant percentage in the sample and the symbol of the dopant. For instance, Rods_5Mn is a CeO₂ sample prepared with hydrothermal synthesis, doped with 5% molar Mn.

3.3. Co-precipitation synthesis

This method occurs in a liquid solution where, the solid formed is called the 'precipitate'. So, the chemicals that causes the formation of the solid are called the 'precipitant'. The formation of a product happens either because of a chemical reaction or because the concentration of a compound exceeds its solubility limit in the host solid. In case there is a rapid quenching or insufficient mixing, diffusion can lead to phase and compositional segregation into the precipitates.

An example of precipitate and precipitant are shown in **Figure 10**:

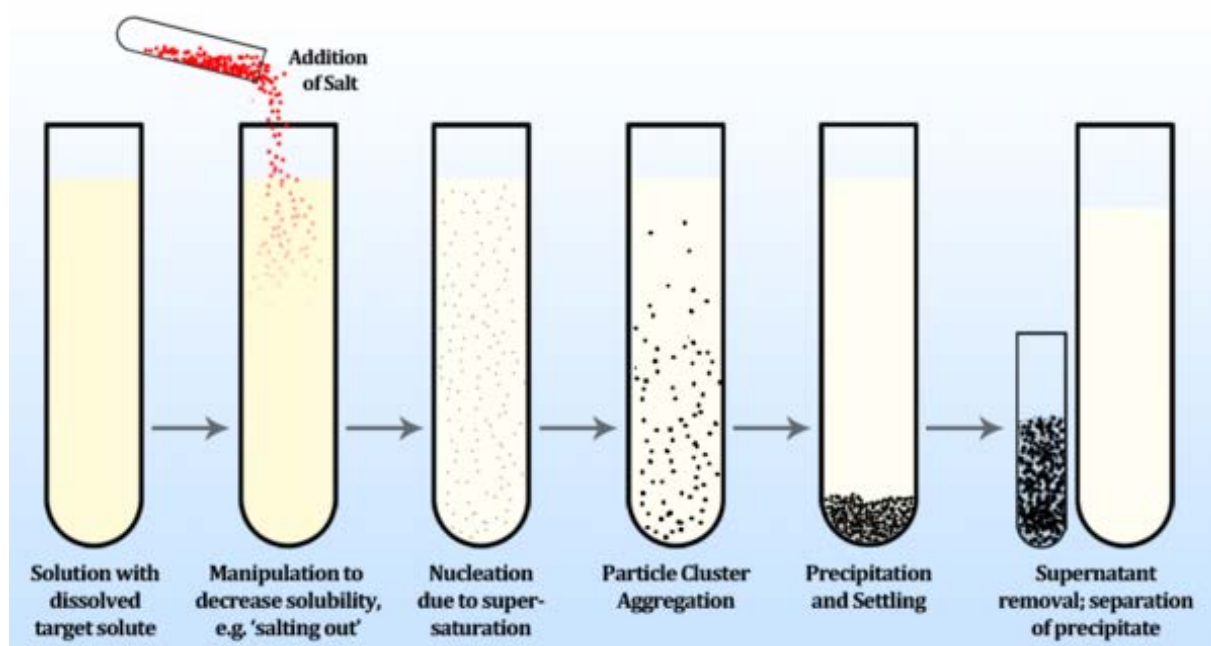


Figure 10: Example of a coprecipitation synthesis procedure.

3.3.1- Catalyst preparation

For this experiment we will dissolve in water a precursor, pure $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, purity 99%) with a metal as dopant such manganese (Mn), copper (Cu) and iron (Fe) with different loadings. The molar fraction for ceria is 95% or 90% and 5% or 10%weight respectively for the dopant.

The dopants that were chosen are in nitrate form: $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich)), iron $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich)) and manganese (II) $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich)).

The solvent we chose for this experiment is water because later the pH solution will be adjusted with ammonia. Due to the lack of information that we were able to find in literature, some adjustments and experiments we done to find the best procedure.

For this synthesis we started from 2ml of ammonia solution (NH_3 in H_2O , 25%wt, Sigma-Aldrich) whose concentration was 13M.

For this process we have the following main steps:

Reaction step

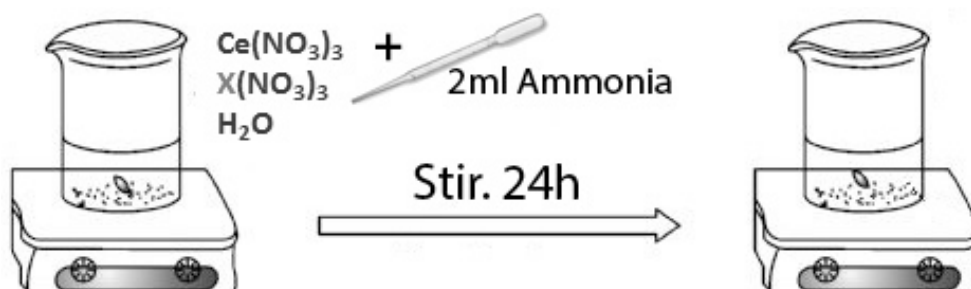


Figure 11: Reaction step of the coprecipitation synthesis, where the precursor and the dopant are dissolved and its pH is controlled by the addition of ammonia.

As **Figure 11** shows, the Ce precursor and the dopant precursor were dissolved in 20ml of deionized water in a beaker with a vigorous stirring. Afterwards, the ammonia was added drop by drop until the 2ml were fully added and pH=9 was reached. The product started to appear immediately as a precipitate. Depending on the dopant, the solution color will be different: brown for manganese, red for iron and green for copper. The solution was kept stirring for 24h to make sure the reaction is finished and the Ce and the dopant precursor are homogeneously mixed.

Washing + dry step

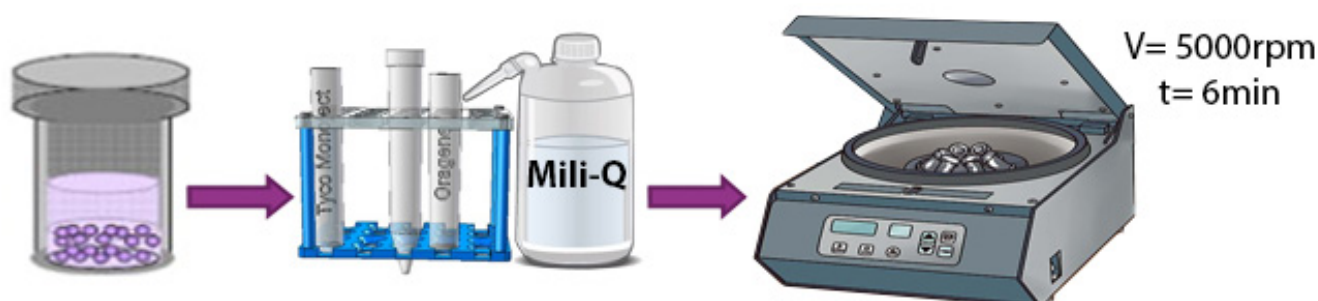


Figure 12: Washing step of the coprecipitation synthesis, where the mixture is washed with milli-Q water several times with a centrifuge.

This procedure is very similar to hydrothermal synthesis step, as reported in Section 3.2.1. As **figure 12** shows, we use a centrifuge for washing our samples three times but this time milli-Q water was used to eliminate the anionic impurities for 6min and 5000rpm each time instead of deionized water and ethanol.

Then, the samples were dried, and for that step an oven was used at 70°C for 24h instead of 2h. This time more time was required because the coprecipitation method yielded samples that are wetter than using hydrothermal synthesis.

Calcination step

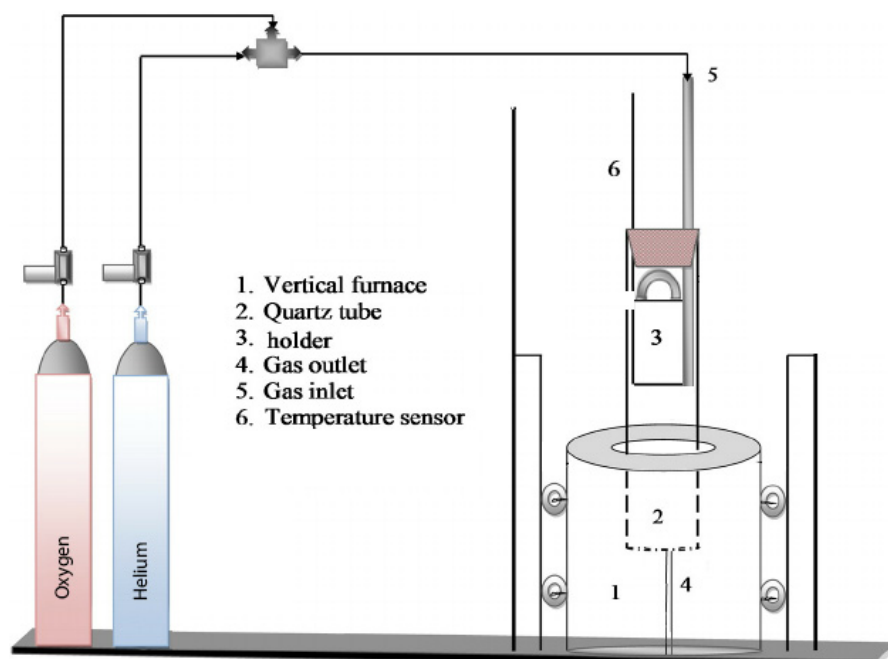


Figure 13: Scheme for the calcination oven that was used for calcinate the catalysts in the coprecipitation synthesis.

As the **figure 13** shows, afterwards, the catalysts were calcined in the calcination oven for 4h in air at 500°C in an 80/20 He/O₂ flow at ambient pressure for 3h. We followed the same procedure that we followed for the products of hydrothermal synthesis.

For the sake of simplicity, the samples synthesized with the coprecipitation method will be defined as Coprecipitation, followed by a number identifying the dopant percentage in the sample and the symbol of the dopant. For instance, Coprecipitation_5Mn is a CeO₂ sample prepared with coprecipitation synthesis, doped with 5% molar Mn.

4. CATALYST CHARACTERIZATION METHODS

In this chapter the different techniques that were used to characterize the catalysts will be explained. We used three techniques: nitrogen physisorption, XRD and TEM.

4.1. Nitrogen physisorption

The specific surface area and the pore size distribution are fundamental parameters for the characterization of the solid. Properties such as porosity, strength, hardness, permeability and thermal stress resistance can be directly correlated to the porous structure of a material. All those properties can easily be investigated by this technique. Surface area can influence the catalytic performance of a material: in heterogeneous catalysis, a higher surface means a higher chance of adsorption of the reactants, which then leads to a higher conversion.

4.1.1. BET theory

It is known that gas molecules adsorb onto solid surfaces that are in their proximity. The Brunauer, Emmett and Teller theory (BET) uses this process to develop a mathematical model to calculate the surface area of a material.

The specific surface area of a catalyst is estimated from the amount of nitrogen adsorbed in relation with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. So, the measurement process involves chilling the surface of the measured catalyst, using nitrogen to adhere to the surface where this process is called adsorption. Once the surface warms up again, the adsorbed species leave the surface, and this process is called desorption.

For our catalysts, surface areas were measured with a Micromeritics Tristar II BET apparatus by nitrogen physisorption at -195°C after an overnight pretreatment of the sample under nitrogen flow at 120°C. Particle sizes were calculated via

$$d_{\text{BET}} = \frac{6}{A_s \times \rho_p}$$

assuming that all particles are spherical. Here, A_s represents the surface area determined by the BET model, and ρ_p represents the density of the material.

4.2. X-Ray diffraction (XRD)

This is a unique method for the determination of crystallinity of a compound. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample: the x-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d\sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

For our catalysts XRD analysis was carried out on a Bruker D2 Phaser using Cu K α -radiation ($\lambda = 1.540184$ Å). With a step-size of 0.020° and a time per step of 0.5 s, 2 θ angles from 10° to 90° were

measured. The sample analysis was performed by the use of the software DiffraCeva and the patterns were indexed according to the PDF database.

4.3. Transmission electron microscopy (TEM)

This technique (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. Using electrons as “light source” and their low wavelength makes possible to get a resolution of thousand times higher than with a light microscope.

It can study different materials down to near atomic levels because can see objects to the order of a few angstrom (10^{-10}m).

For our catalyst, TEM measurements were performed on a FEI Tecnai 20 electron microscope at an electron acceleration voltage of 200 kV with a LaB₆ filament. A few milligrams of sample were ultrasonicated as described above and dispersed over a carbon-coated Cu grid. Particle counting was performed with the software ImageJ, by analyzing images that represent different regions of the sample. The average particle size and particle size distribution were determined by measuring around 100 particles for each sample.

5. CATALYTIC ACTIVITY IN SOOT OXIDATION

As known from experimental evidence, soot particles are released from diesel engine exhausts and they are really dangerous for the environment and health. These particles can cause several problems like allergic, respiratory and cardiovascular diseases. That's why this reaction is being studied just to decrease such a problem controlling this emissions by catalytic conversion of the particles to harmless CO_2 and H_2O .^{[1],[2],[14]}

This reaction was carried out in air flow using a thermogravimetric analyzer (TGA) from room temperature to 900°C by increasing the temperature with a constant heating rate.

This technique provided us with data about the standard oxidation temperature of soot without a catalyst, and the extent of the decrease of the oxidation temperature when a catalyst is added.

We used this technique in order to compare the results of the different preparation methods such as flame spray pyrolysis (FSP)^[13], hydrothermal synthesis and co-precipitation with different metals as dopants.

In order to replicate soot, we used a commonly employed carbon material, called Printex U.

Procedure

- Fill the TGA sample holders with the soot and catalyst mixture. Write down the exact weight of the mix without the pan.
- Put the sample holders inside the TGA.
- Choose the right method. In this step we use a previously developed method, which starts from room temperature and heats the sample in a 20/80 O_2/He mixture with a ramp of $10^\circ\text{C}/\text{min}$ until 900°C
- Write down the initial weight of the sample.

First of all a validation of the method for the soot is needed because we don't know if the experiment can be reproducible.

5.1. Validation of the soot method

For this experiment we used 4 sample holders and they were filled only with soot, without catalyst.

5.2. Validation of the ratio method

Once we know the method is good and reproducible, we need to find the optimal ratio between the soot and the catalyst we can use. This experiment we tried with (1:5) and (1:2) ratios catalyst and soot respectively. In order to have a reference about the weight% loss, the soot without catalyst was included in the figures.

▪ Low ratio (1:5)

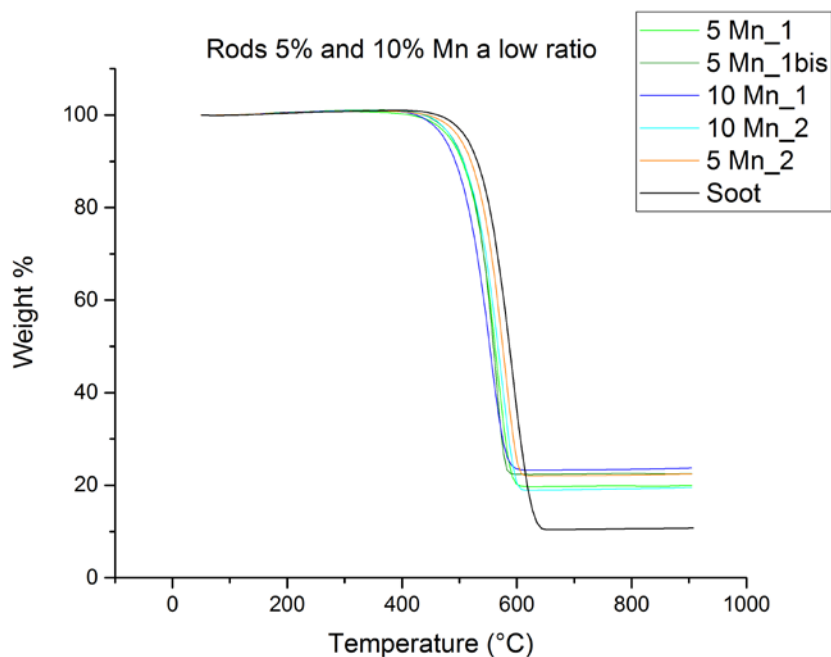


Figure 14: Graphic of a catalytic activity for a soot oxidation reaction using low ratio for the soot and the mixture of catalyst.

As the **figure 14** shows, the low ratio between the soot and the catalyst is not good because they should have the same or very similar lose of weight and that's not the case. Even for the same samples were made twice have different lose of weight.

▪ High ratio (1:2)

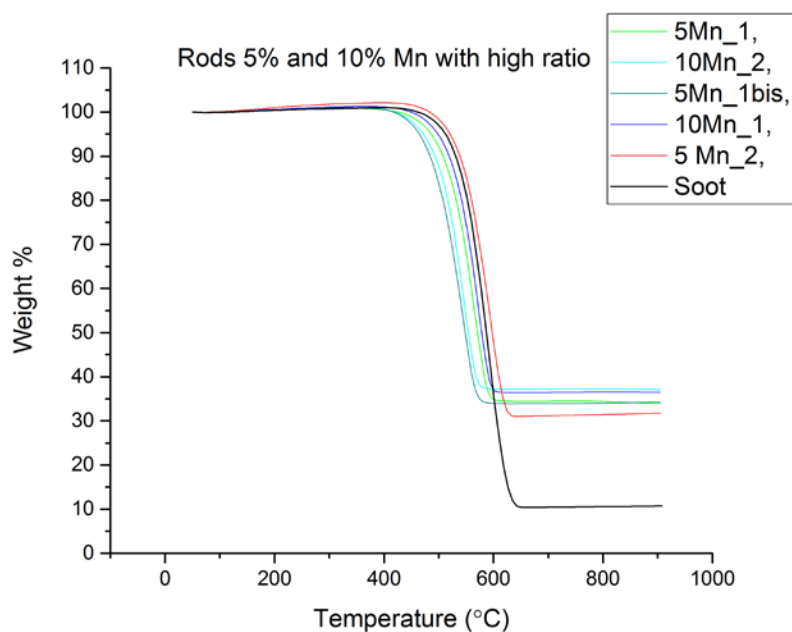


Figure 15: Graphic of a catalytic activity for a soot oxidation reaction using high ratio for the soot and the mixture of catalyst.

However as the **figure 15** shows, a high ratio of (1:2) is good enough and the results are credible. We synthesized twice each catalyst and we labelled them with 1 or 2 in the end depending on the sample and we repeated one and we called it with the same name but adding bis in its name. The 10%weight manganese have similar lose of weight and the 5%Mn have similar lose of weight between them. The 5Mn_2 may be an outlayer because for preparing the samples for the TGA we are weighing the soot and the catalyst and we are talking about a few miligrams. So, it is high likely that this particulary one was not weight correctly.

6. CALCULATIONS, RESULTS AND DISCUSSION

In this chapter a summary of the results that were obtained for each method with different metal as dopants and different metal loadings will be discussed.

6.1. Nitrogen physisorption

With this characterization for the catalyst, we can study different properties such as porosity, surface area and particle size. The latter can be calculated with the following equation:

$$d_{\text{BET}} = \frac{6}{A_s \times \rho_p}$$

The main properties we are interested to study on the catalysts are surface area and particle size. Higher surface area means higher chance of adsorption of the reactants leading to a higher conversion and small particle size means high chances to have higher dispersion, so our catalyst will be more reactive.

Tabel 1: Preliminary results from nitrogen physisorption for FSP synthesis.

Sample	BET area (m ² /g)	Particle size (nm) (BET)
FSP_2,5Mn	180	5
FSP_5Mn	174	5

For the flame spray pyrolysis-made samples, the results show a very high surface area, as high as 180 m²/g, which is a remarkable value for a low surface area material as CeO₂. The high surface area is matched by an unusually small particle size of 5 nm (calculated with the formula reported above).

$$\begin{aligned} \text{Average BET area} &= 177 \text{ m}^2/\text{g} \\ \text{Particle size} &= 5 \text{ nm} \end{aligned}$$

These results mean nitrogen physisorption gives us good results for flame spray pyrolysis with high BET surface area and small particles, making those materials good candidates for catalysis.

Table 2: Preliminary results from nitrogen physisorption for coprecipitation synthesis.

Sample	BET area (m ² /g)	Particle size (nm) (BET)
Rods_5Mn	61	14
Rods_10Mn	61	14
Rods_5Fe	50	18
Rods_10Fe	46	15
Rods_5Cu	77	11
Rods_10Cu	76	11

However, for hydrothermal synthesis, the preliminary results we got for BET surface area and particle size were not as good as expected as **table 2** shows. We performed the experiment for nanorods doped with different metals and for all experiments we got a low BET surface area and a high particle size.

$$\text{Average BET area} = 62 \text{ m}^2/\text{g}$$

$$\text{Particle size} = 14 \text{ nm}$$

Therefore, hydrothermal synthesis yields particles with a smaller surface area and a bigger particle size.

Table 3: Preliminary results from nitrogen physisorption for hydrothermal synthesis.

Sample	BET area (m ² /g)	Particle size (nm) (BET)
Coprecipitation_Ce	93	12
Coprecipitation_5Mn	130	10
Coprecipitation_10Mn	125	9
Coprecipitation_5Fe	112	7
Coprecipitation_10Fe	119	9
Coprecipitation_5Cu	106	8
Coprecipitation_10Cu	114	8

For coprecipitation, the results we got for particle size and BET surface area were as good as for flame spray pyrolysis as we can appreciate in **table 3**.

$$\text{BET area} = 112 \text{ m}^2/\text{g}$$

$$\text{Particle size} = 8 \text{ nm}$$

So, these catalysts having a high BET surface area and a small particle size suggests that they might be more reactive than the catalysts made by hydrothermal synthesis. Besides that fact, this method is simpler and less time-consuming than FSP.

6.2. X-Ray diffraction (XRD)

This method will allow us to see the determination of crystallinity of a compound. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample as it is explain in Chapter 4.3:

For our catalysts XRD analysis was carried out on a Bruker D2 Phaser using Cu K α -radiation ($\lambda = 1.540184 \text{ \AA}$). With a step-size of 0.020° and a time per step of 0.5 s, 2θ angles from 10° to 90° were measured. The sample analysis was performed by the use of the software DiffracEva and the patterns were indexed according to the PDF database.

In this section we report the XRD patterns of a choice of samples.

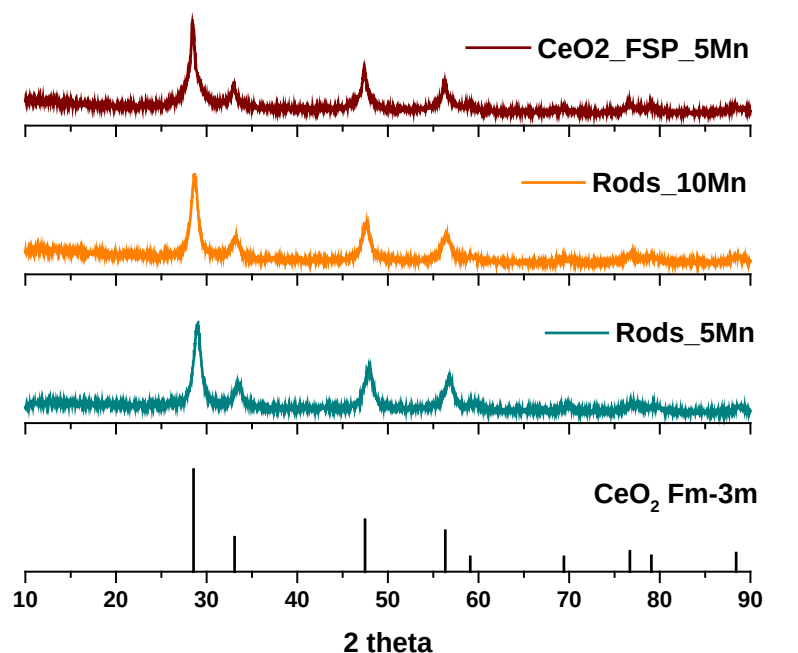


Figure 16: XRD analysis for FSP and hydrothermal synthesis being compared with the standard CeO₂ from the instrument library.

The XRD characterization for the catalysts synthesized with flame spray pyrolysis and hydrothermal synthesis is shown in **figure 16**.

As we can see in the figure, we obtained the same peaks for pure ceria made it by flame spray pyrolysis and the catalysts that were made by hydrothermal synthesis.

The peaks can be ascribed to pure CeO₂ (cubic fluorite phase, space group FM-3m), as shown in the bottom spectrum of **Figure 16**. That suggests that there are no traces of manganese-rich phase in these catalysts. The broader shape of the peaks in the XRD patter of the sample prepared with FSP is due to the presence of extremely small nanoparticles.

The regular shape of the peak suggests that the level of crystallinity of the catalysts is high.

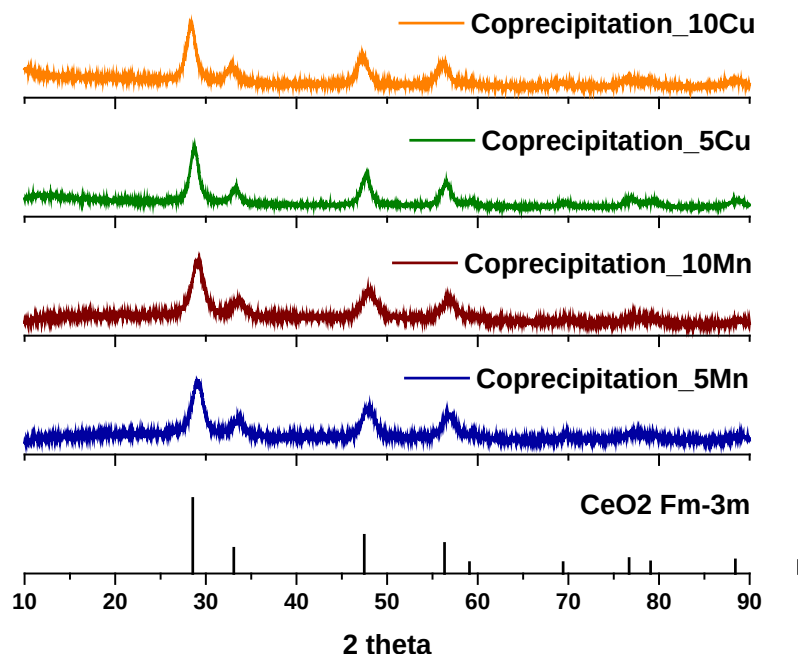


Figure 17: XRD analysis coprecipitation synthesis.

As we can see in **figure 17** for the coprecipitation synthesis we got the same peaks: shape, size and position. They can all be ascribed to the presence of pure CeO_2 , as shown in the bottom spectrum and as discussed before.

As the **figure 17** and **figure 16** showed us, there is no evidence of traces of manganese or copper-rich phases. So, the metals were chosen as dopant are well dispersed.

6.3. Transmission electron microscopy (TEM)

This technique (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light.

For our catalyst, TEM measurements were performed on a FEI Tecnai 20 electron microscope at an electron acceleration voltage of 200 kV with a LaB_6 filament. A few milligrams of sample were ultrasonicated as described above and dispersed over a carbon-coated Cu grid. Particle counting was performed with the software ImageJ, by analyzing images that represent different regions of the sample. The average particle size and particle size distribution were determined by measuring around 100 particles for each sample.

6.3.1- Flame spray pyrolysis (FSP)

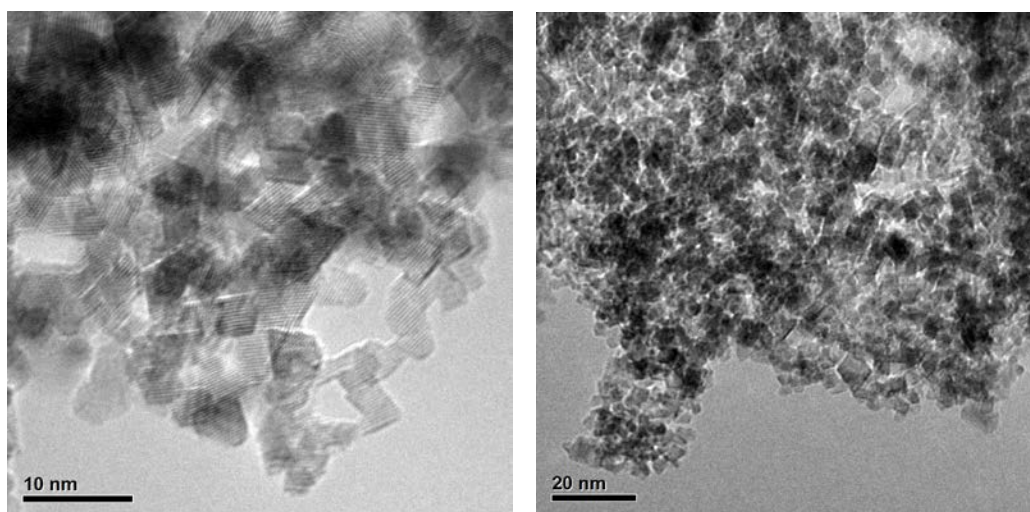


Figure 18: TEM pictures of FSP_5Mn

For the catalysts made by flame spray pyrolysis (FSP) with a 5% of the mole fraction of manganese, the average of particle size is the following one:

Average particle size: 3.8 ± 1 nm

So, catalysts with small particles is one of the factors that makes those materials good candidates for catalysis.

As **figure 18** shows, the particles are quite homogeneous in size and have a shape called nanopolyhedra.

6.3.2- Hydrothermal synthesis

Due to high number of catalysts synthesized and time constraints, we report this characterization at least once per catalyst with different metal.

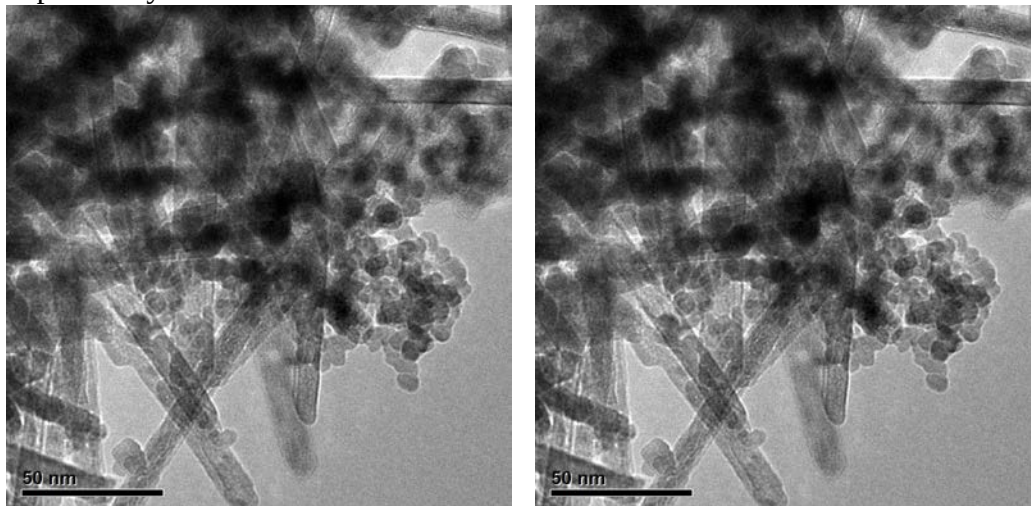


Figure 19: TEM pictures of Rods_5Mn

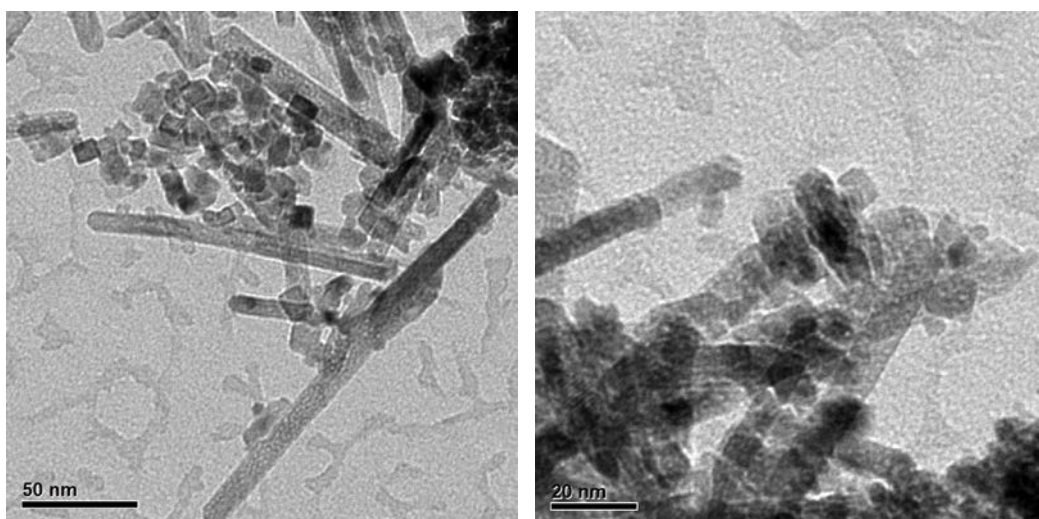


Figure 20: TEM pictures of Rods_5Cu

Using hydrothermal synthesis making the catalyst with 5% of the mole fraction of the dopant, we obtained an average of particle size bigger than for flame spray pyrolysis, by the use of the BET particle size calculation method:

Average particle size (Rods_5Mn): 14 ± 2 nm

Average particle size (Rods_5Cu): 14 ± 2 nm

Here we see that TEM provides us with many more details than the BET method. For instance, we can see that the average particle size calculated with the BET method is not accurate here, since these samples

are not spherical in shape, but many of them have a rod-like morphology. In this situation, TEM represents a better choice to evaluate the particle size of these catalysts.

As we used an specific method for hydrothermal synthesis for obtaining nanorods, we should expect that shape for our catalyst but as the **figure 19** and the **figure 20** shows, this time we got a mix of two shapes: nanorods and polyhedral.

The Mn and Cu-doped nanorods present a disrupted structure, compared to the pure CeO₂ nanorods (here not reported). This means that the inclusion of transition metals in the structure is able to deeply influence the final product.

6.3.3- Coprecipitation synthesis

Due to high number of catalysts synthesized and time constraints, we report this characterization at least once per catalyst with different metal.

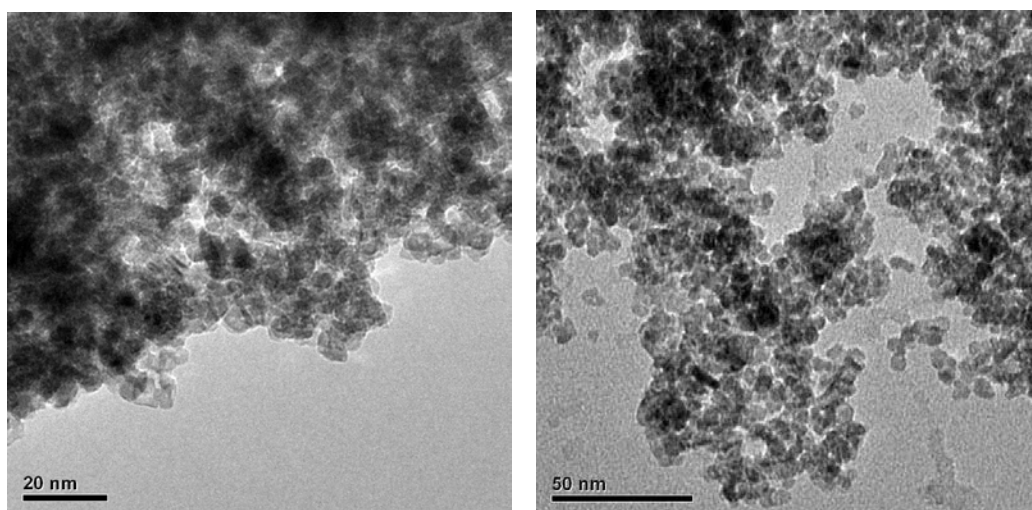


Figure 21: TEM pictures of Coprecipitation_5Mn

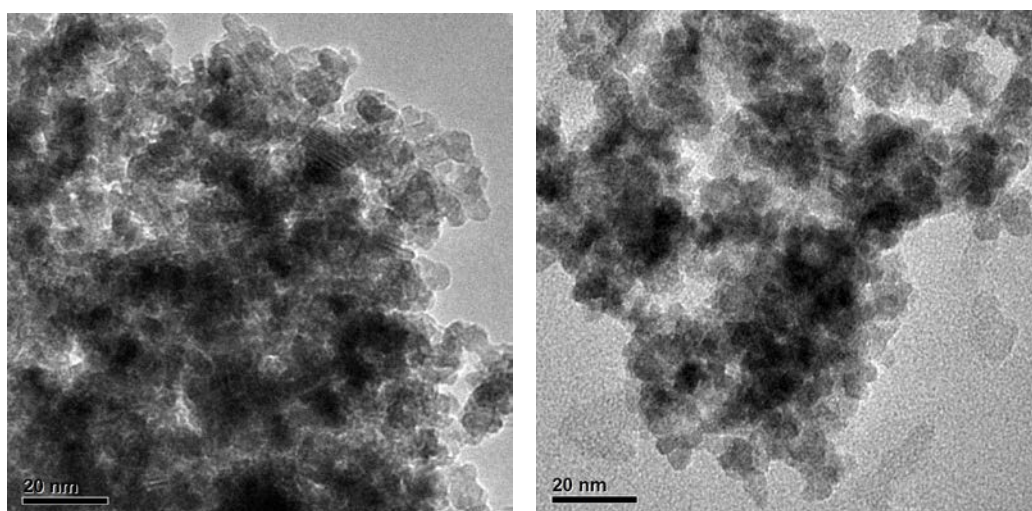


Figure 22: TEM pictures of Coprecipitation_5Cu

However, using coprecipitation synthesis making the catalyst with 5% of the mole fraction of the dopant, we obtain an average of particle size bigger than for hydrothermal synthesis but alike to flame spray pyrolysis:

Average particle size (Coprecipitation_5Mn): 5.8 ± 1 nm
 Average particle size (Coprecipitation_5Cu): 7.4 ± 2 nm

So, small particles means high surface area and for the consequence those materials are good candidates for catalysis.

Besides that, we don't have a mix of shapes as we got for hydrothermal synthesis. The catalysts have a shape similar to cubes and nanopolyhedra as the **figure 21** and the **figure 22** shows.

6.4. Catalytic activity in soot oxidation

This characterization is the one who will give us the final conclusion for the catalyst.

As it was explained before in the abstract, introduction and a bit deeper in Chapter 5, soot particles are released from diesel engine exhausts and they are prejudicial for environment and health.^[2]

So, with this characterization we will be able to see with which synthesis and metal as dopant are better at decreasing the oxidation temperature when the catalyst is added to the soot.^[14]

This reaction was carried out in air flow using a TGA from room temperature to 900°C by increasing the temperature with a constant heating rate.

In order to replicate soot, we used a commonly employed carbon material, called Printex U.

6.4.1- Flame spray pyrolysis (FSP)

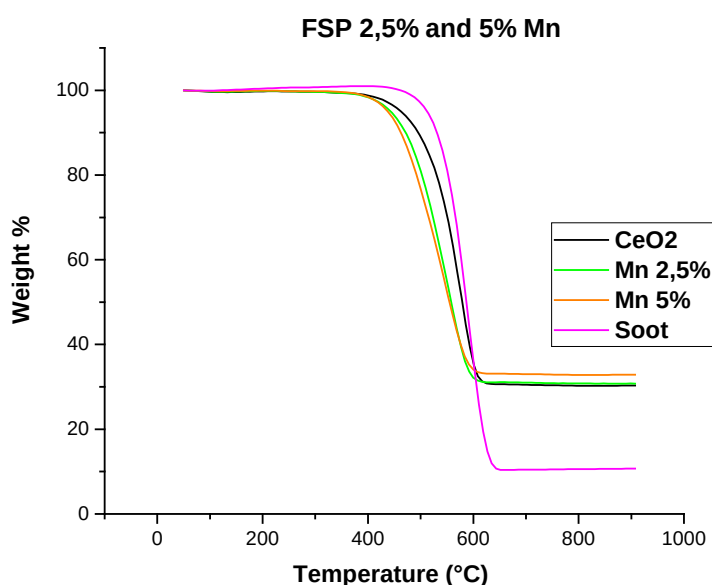


Figure 23: Catalytic activity in soot oxidation with FSP and manganese as dopant.

As **figure 23** shows, flame spray pyrolysis could be a good method to synthesize the catalyst because even only adding a mixture of pure ceria catalyst to the soot we can already see there is a decrease in the oxidation temperature.

However, when a mixture of catalyst with manganese as dopant is added to the soot, there is a higher decrease of the oxidation temperature, making those catalyst even better.

6.4.2- Hydrothermal synthesis

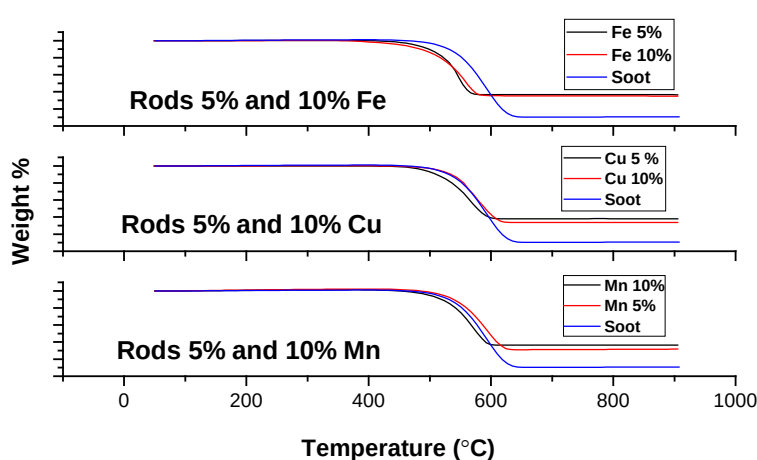


Figure 24: Catalytic activity in soot oxidation with hydrothermal synthesis and different metals as dopants.

As **figure 24** shows, hydrothermal synthesis could be a good method to synthesize the catalyst but not as good as the ones made by flame spray pyrolysis. For both metal loadings 5% and 10% of each metal we got a decrease of the oxidation temperature. However, using iron as a dopant this temperature is even lower than using manganese or copper making those catalyst even better for being used for catalytic soot oxidation.

6.4.3- Coprecipitation synthesis

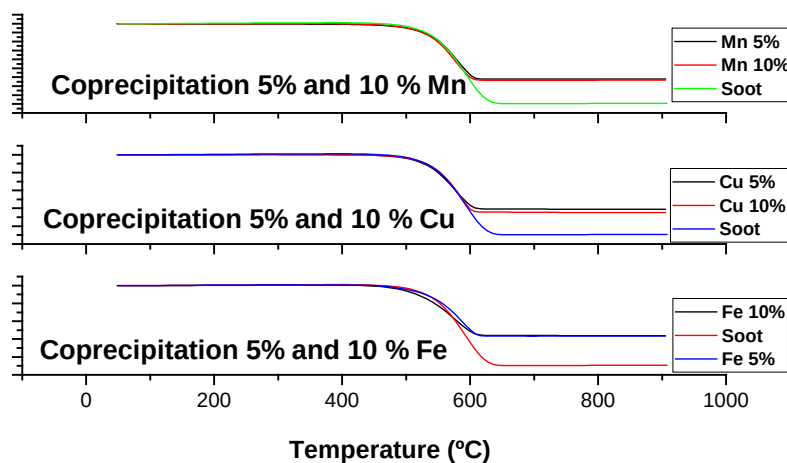


Figure 25: Catalytic activity in soot oxidation with coprecipitation synthesis and different metals as dopants.

Besides the good results we got in BET surface area, XRD, and particle size for those catalysts as *figure 25* shows, coprecipitation synthesis may be not the best method to synthesize the catalysts.

As we can see, with those catalyst there is no decrease of the oxidation temperature either with manganese, copper or iron and it doesn't matter the percentage of the molar fraction they are present in the catalyst.

So, this procedure of synthesis is the worst one comparing it with flame spray pyrolysis and hydrothermal synthesis.

7. CONCLUSION

The aim of this project was to find the best catalyst for the catalytic soot oxidation reaction. Moreover the following project introduces main different objectives that needed to be solved.

The performance of CeO_2 catalyst was studied with three different transitions metals of varying size and reducibility such as copper, iron and manganese as dopants and with different molar ratio 5% and 10% per each metal.

- The accuracy study concludes that the soot was used has similar values and results when it has done several times with the same TGA procedure. So, we can confirm that our method with the soot chosen and with the TGA procedure is a reproducible method for the soot oxidation reaction. Therefore, the precision of the instrument was proved. Moreover, this method used for testing the catalysts were validated by carefully choosing the ratio of catalyst soot, where this ratio was (1:2).

However, the study should be continued by testing the chosen ratio and validating it if the method is reproducible with real soot. Nevertheless, to simplify this project and for not having on time the real soot, it has been decided to use the Printex U soot for this experiments.

- The comparison between the three different synthetic routes used for our catalyst: flame spray pyrolysis (FSP), hydrothermal synthesis and coprecipitation have the goal to find the best catalyst for the activity soot oxidation reaction. The obtained results show us an encouraging solution using flame spray pyrolysis synthesis, where independently of the metal loading, there is an important decrease of the oxidation temperature. Moreover, using TEM, XRD and BET surface area as characterization methods, we found a high surface area and small particles making those catalysts reactive and good for this purpose.

Although, the obtained results for hydrothermal synthesis were not as good as for FSP synthesis they showed a good reactivity with the soot and a significant decrease of the oxidation temperature making iron the best metal as a dopant. Nevertheless, those catalysts had a smaller BET surface area and a bigger particle size.

However, for the coprecipitation synthesis was the opposite. The obtained results for XRD, TEM and BET surface area were similar to the flame spray pyrolysis synthesis with a high surface area and a small particle size. Although the most important results are from the activity soot oxidation reaction where in this case the catalysts showed a non-reaction performance with the soot making these catalysts useless for this purpose.

However, the study should be continued by testing those catalyst with real soot, in order to simulate a more realistic reaction environment. Real soot has different components than the Printex U soot that was used, therefore some catalysts might prove to have a different reactivity.

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This internship made me realize the importance of having a good English level and a good background in my studies, that's why I extended my enrollment. Opportunities like this you cannot let them escape and that's why the second part of my acknowledgements is for Emiel Hensen. He is the person who made this possible giving me chance to stay 1year studying and doing some experiments in the IMC department. Thanks a lot, for giving me this opportunity.

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