

# Production of a catalyst support in supercritical fluid

## Production of pure and doped ceria

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### Abstract

The present thesis had as objective to synthesize and characterize a catalyst with particles with nanometric dimensions, namely a ceria-zirconia oxide catalyst.

The catalyst was produced under supercritical conditions and characterized with X-Ray Diffraction, Transmission Electron Microscopy, Inductively Coupled Plasma and BET analysis.

Different parameters were studied as the effect of the solvent, the effect of the quantity of cerium in the catalyst and finally the effect of the residence time of the synthesis. For the analyse of the effect of solvent, two solvents were used namely distilled water and propanol. For the case of the study of the effect of the quantity of cerium, there was the substitution of cerium with zirconium ( $Ce_{1-x}Zr_xO_2$  -  $x=0; 0,25; 0,50; 0,75; 1$ ) using distilled water as solvent. The residence times used in this study were of 10s, 30s and 60s.

From these characterizations, it was possible to conclude that when propanol is the solvent the particles are smaller and that with the increase of residence time there is an increase of the crystallite size. It is also worth to note that the particles are single crystals.

As for the study of the composition of the catalyst, a small effect of the Zr content was observed in the particle size of the catalyst. In relation to the specific surface area, the produced catalyst presented a range of values from 130 m<sup>2</sup>/g to 230 m<sup>2</sup>/g, with an increase of this value with a decrease of cerium percentage.

**Keywords:** ceria; ceria-zirconia; catalyst; supercritical; solvothermal; synthesis

## 1. Introduction

Nanoparticles of CeO<sub>2</sub> have been used as catalyst to produce hydrogen, by introducing zirconium to its crystal lattice will allow the control of the properties of the catalyst. So, a Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalyst is produced. This catalyst has a high oxygen storage capacity (OSC), thermal stability, high surface area and high capability of H<sub>2</sub> uptake. Also, cerium-zirconium mixed oxides promote the water-gas shift reaction that occurs during the production of hydrogen. [1-8]

One of the techniques to produce cerium-zirconium mixed oxides is solvothermal synthesis in supercritical medium.

Supercritical state is defined as the domain at which the distinction between the liquid state and the gaseous state disappears and the material exists as a fluid. [9] This is obtained when the critical point is reached, which has as coordinates the critical temperature (T<sub>c</sub>) and the critical pressure (P<sub>c</sub>). [10-12] Some advantages of using supercritical fluids (SCFs) are high diffusion rates, low viscosity, adjustable density, high miscibility with gases and high diffusion rates. [11, 13] Another one is the fact that the properties of the reaction medium are able to be adjust at will with slightly variations in pressure and/or temperature. [9, 10, 13] The use of this technique allows the achievement

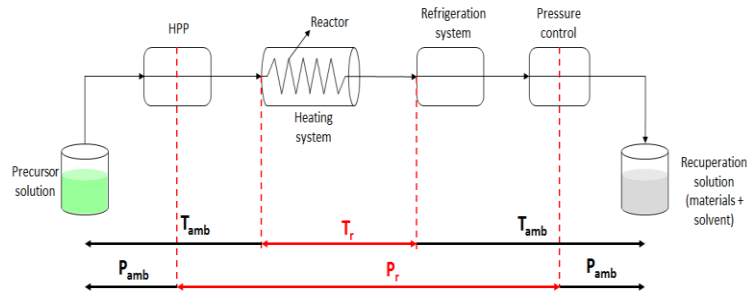
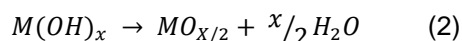
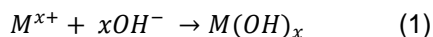


Figure 1 Experimental set-up

of a product dry and clean in a one step process, making it possible the avoidance of purification stages and large particle agglomeration. Also, because of the easy control of the method is easier to control the characteristics of the catalyst produced.

This method is composed by two parts: the Hydrolysis (Eq. 1) and the Dehydration (Eq. 2). So when a metal aqueous solution is heated up, metal hydroxides are formed due to shift of reaction equilibrium. At higher temperatures, the equilibrium shifts further toward the metal oxide formation. [12, 14, 15]



In order to produce a catalyst composed by nanoparticles, it is important to consider the supersaturation degree. This phenomenon happens when the solubility of the metal oxide is low. So, when mixing metal aqueous solution with SCF, it is generated an extremely high degree of supersaturation and it happens rapid nucleation at the mixing point, promoting the precipitation of the nanoparticles. [12]

## 2. Experimental details

All the chemical compounds used were of the brand *Sigma-Aldrich*. The precursors chosen were Ammonium Cerium Nitrate ( $Ce(NH_4)_2(NO_3)_6$ ) with an assay of 98,5% and Zirconium Oxynitrate Hydrate ( $ZrO(NO_3)_2 \cdot xH_2O$ ) with an assay of 99%.

### 2.1 Catalyst preparation

The catalyst support was produced using water and propanol as solvent and applying a residence time of 10, 30 and 60s. The operating pressure was 24,5 MPa and the

concentration of the precursor solution of 0,01 M. For water as solvent, the temperature used was 400°C and for propanol 300°C.

The values of x used for  $Ce_{1-x}Zr_xO_2$  catalyst support were 0, 0,25, 0,50, 0,75 and 1.

The set-up used can be seen in Figure 1, where HPP is a high pressure pump,  $T_{amb}$  and  $P_{amb}$  are the room temperature and pressure, respectively and  $T_r$  and  $P_r$  are the reactor temperature and pressure, respectively. The final solution is then centrifuged, filtered and let to dry to obtain the catalyst.

### 2.2 Characterization

The catalysts produced was characterized through characterization techniques such as X-Ray Diffraction (XRD), BET analysis, Transmission Electron Microscopy (TEM) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES). With the XRD characterization was possible to observe the XRD pattern, calculate the crystallite size and the lattice parameter. The BET analysis allowed to know the specific surface area of the catalyst. By using TEM, it was obtained an image of the particles of the catalyst, being consequently possible to get by measure the average particle size. The ICP technique provided the concentration of cerium in the catalyst, in order to compare with the expected value.

## 3. Results and discussion

The sample names have the following configuration: Solvent-Percentage of Cerium-Temperature-Residence time. For the solvent, W represents distilled water and Pr 1-propanol. The unit for temperature is °C and for residence time is seconds (s).

### 3.1 Effect of solvent in ceria synthesis

The x-ray diffraction patterns of the sample of CeO<sub>2</sub> obtained by the solvothermal

propanol and 90 particles for water. So, for propanol, the sample as a sphere morphology and a size of  $3,7 \pm 0,7$  nm. For water, the morphology is of a “peanut” with a

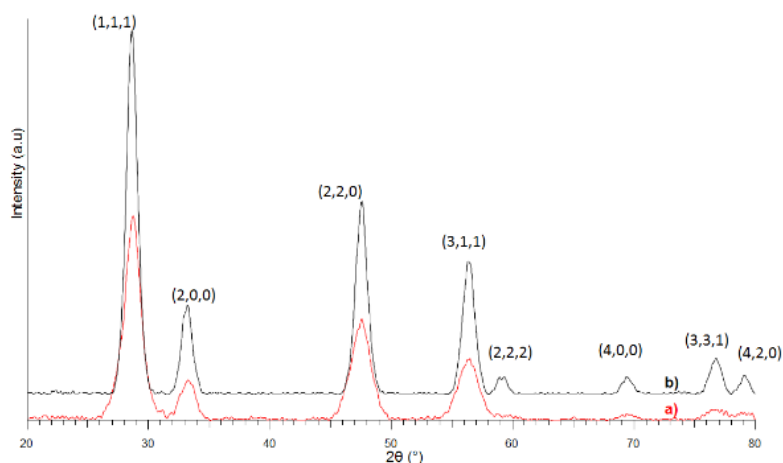


Figure 2 XRD patterns with the indexing values (h,k,l) of ceria. a) Pr-100-300-60, b) W-100-400-30

method under supercritical conditions are shown in Figure 2. The solvents used were propanol and distilled water.

The crystallite size and lattice parameter a calculated was 4,8 nm and 5,408Å for propanol and 6,7 nm and 5,413Å for water. Comparing the values, it is possible to see a difference between the crystallite sizes where the smaller one is achieved when the solvent is propanol. For the lattice parameter, the values are similar.

XRD patterns allowed to confirm that the ceria prepared had the same crystal structure as pure ceria (cubic), due to the fact that the peaks correspond to the ones expected for this material.

size of  $5,2 \pm 0,7$  nm. The “peanut” morphology is due to sintering during the analysis. As it happened for the crystallite size, there was a decrease in size when propanol was used as solvent.

### 3.2 Effect of composition

Ceria was doped with zirconium using water as solvent and a residence time of 30s.

An ICP analysis was realized to compare the theoretical percentage of cerium in the catalyst support with the experimental. The result can be seen in Table 1.

There is a slightly difference between the values in Table 1 that increases with the increasing percentage of zirconium. This

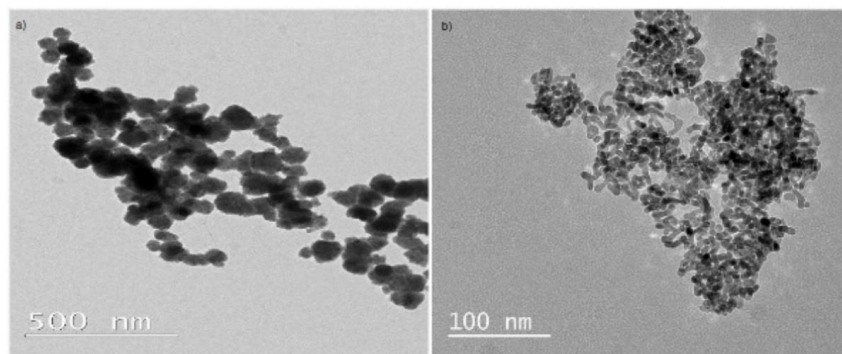


Figure 3 Images of pure ceria samples obtained via TEM: a) Pr-100-300-60, b) W-100-400-60

The TEM results can be seen in Figure 3. From Figure 3, it was determined the average particle size using 180 particles for

may be explained due to the difficulty of dissolving zirconium in distilled water.

A XRD characterization was also done, the pattern obtained can be seen in Figure 4.

Table 1 Comparison between theoretic and experimental percentage of cerium

Sample	Theoretic % of cerium	Experimental % of cerium
W-100-400-30	100	100
W-75-400-30	75	78
W-50-400-30	50	56
W-25-400-30	25	34
W-0-400-30	0	0

(cubic) and that prepared zirconia had the same as pure zirconia (monoclinic).

It is also possible to notice a shift in the characteristic peak of ceria around  $2\theta = 28,542^\circ$  to higher angle values as zirconium contents increases. This outcome is caused by the contraction of the lattice cell parameter when inserting Zr into CeO<sub>2</sub> fluorite lattice.

Again, the crystallite size ( $d_{cr}$ ) and lattice parameter  $a$  was determined. The results are in Table 2.

From Table 2, the crystallite diameter and the lattice parameter calculated decrease

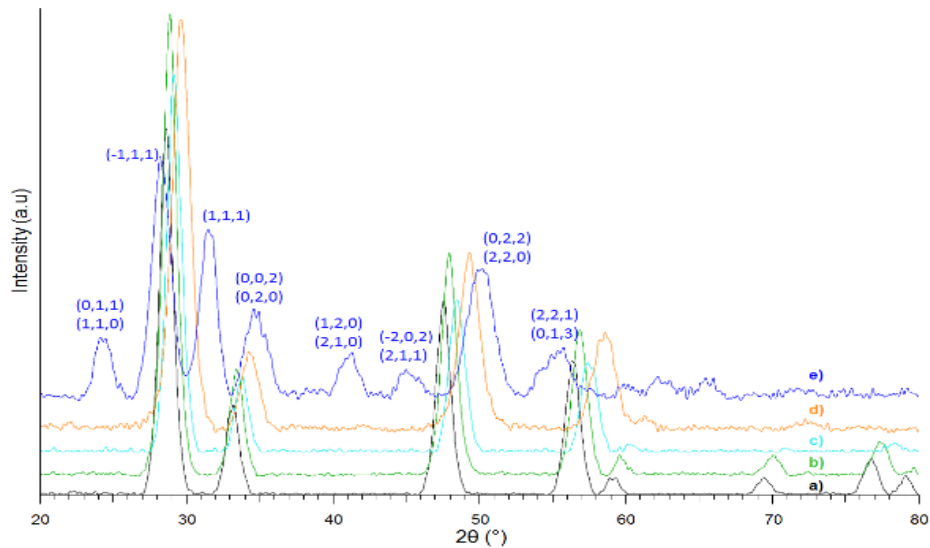


Figure 4 XRD patterns with the indexing values (h,k,l) of zirconia. a) W-100-400-30, b) W-75-400-30, c) W-50-400-30, d) W-25-400-30 and e) W-0-400-30

The XRD patterns allowed to confirm that ceria and ceria-zirconia mixed prepared had the same crystal structure as pure ceria

when the percentage of zirconium increases. This shrinkage of lattice cells indicates that the ions of Ce<sup>4+</sup> with an ionic size of 0,097 nm are substituted by Zr<sup>4+</sup>, which have a smaller ionic size (0,084 nm).

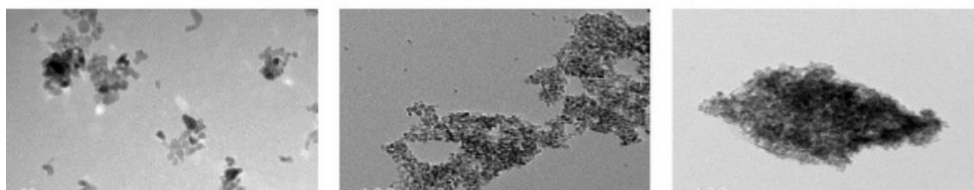
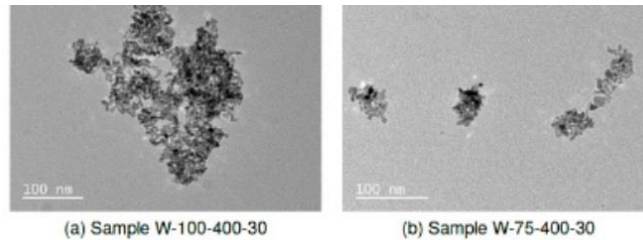


Figure 5 Images of samples obtained via TEM

TEM characterization was also done with the results in Figure 5.

Table 2 Crystallite size and lattice parameter (a) obtain with XRD pattern

Sample	$d_{cr}$ (nm)	a (Å)
W-100-400-30	6,7	5,413
W-75-400-30	6,6	5,365
W-50-400-30	6,2	5,321
W-25-400-30	5,5	5,243
W-0-400-30	5,4	5,123

The particles have a “peanut” morphology and the cluster size decreases with the decreasing of cerium percentage. This may happen because of the pH of the solution. The decomposition of cerium ammonium nitrate yields to the formation of hydrogen ions, reducing the pH of the medium as the value of cerium increases.

The particle average size obtained from TEM is shown in Table 3.

Table 3 Particle average size obtained via TEM analysis

Sample	Particle average size (nm)
W-100-400-30	5,2±0,7
W-75-400-30	4,9±1,3
W-50-400-30	4,0±0,6
W-25-400-30	5,0±0,9
W-0-400-30	4,6±0,9

From this table, a decrease of the size with the increasing amount of zirconium is observable. Although for the last two samples there is an increase and then decreases again. This small variation can be disregarded because of the small number of particles studied and the fact that the

analysis is done by hand increasing the error associated.

The last characterization realized for the study of composition in water was of the specific surface area ( $S_{BET}$ ). This was achieved by doing a BET analysis and the results are in Table 4.

Table 4 Determined specific surface area

Sample	$S_{BET}$ (m <sup>2</sup> /g)
W-100-400-30	229
W-75-400-30	136
W-50-400-30	149
W-25-400-30	169
W-0-400-30	202

As it can be seen the specific surface area is higher when the compounds are pure, especially in the case of ceria. Addressing the doped samples, it is clear that when the amount of zirconium increases the specific surface area also increases.

The increase of the specific surface area with zirconia in the doped samples can also be associated with the decrease of the density of the particles.

It is also important to point that just one test of BET analysis was done for each sample not guaranteeing that the behaviour would be the same if the analysis was repeated, thus justifying the values obtained.

### 3.3 Effect of residence time in water

The effect of residence time was studied using a sample with 50% of cerium and using distilled water as solvent. The residence times analysed were 10s, 30s, and 60s.

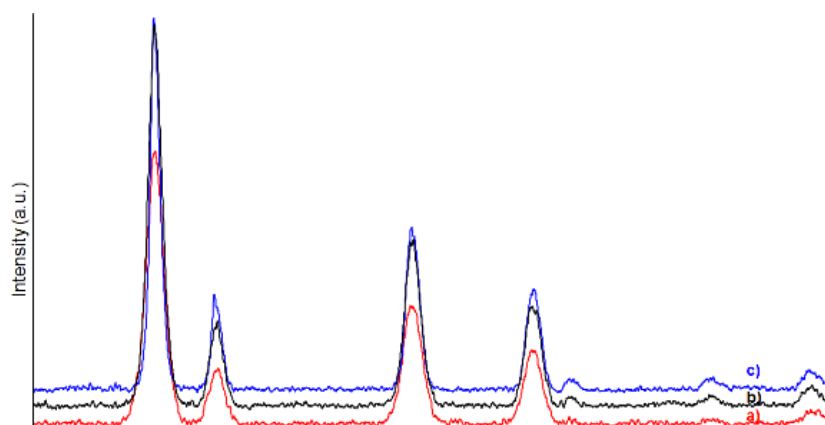


Figure 6 XRD patterns. a) W-50-400-10, b) W-50-400-30, c) W-50-400-60

A XRD study was realized and the result patterns are in Figure 6.

From this figure, a similarity between the patterns in terms of intensity and position of the peaks can be seen. The crystallite size and lattice parameter were also determined. The results obtained were, respectively, 5,0nm and 5,315Å for 10s, 6,2nm and 5,315Å for 30s and 8,7nm and 5,320Å for 60s. With this results, it can be seen that the residence time does not affect the lattice parameter because the crystallite structure of the unit cell is the same for the three cases due to the fact that they have the same composition. There is also an increase in the crystallite size with the increase of residence time. This increment was expected and it is justified by the fact that the particle stays more time in the reactor and so it has the chance of growing for longer time.

### 3.4 Effect of solvent in ceria-zirconia oxide synthesis

The effect of solvent was also realized with a sample with 50% cerium where the solvents used were distilled water and propanol. The residence time for propanol was 40s because of the pump capacity and for distilled water was 30s.

The resulting XRD patterns from this studied can be seen in Figure 7.

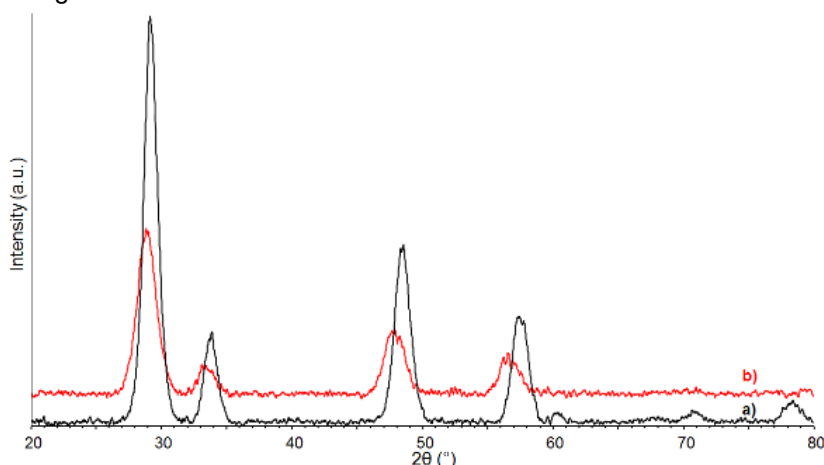


Figure 7 XRD patterns. a) W-50-400-30, b) Pr-50-300-40

The crystallite size determined was 6,2nm for water and 4,3nm for propanol. The lattice parameter calculated was 5,315Å for water and 5,382Å for propanol.

In Figure 7, a shift of the peaks to the left can be seen when the solvent is propanol. As consequence, the values of lattice parameter do not match. This difference may happen because the percentage of cerium when propanol is solvent, could not be the expected due to fact that zirconium may be soluble in propanol, reducing its percentage in the sample.

Also, as it was seen for pure ceria, the crystallite size is smaller for synthesis that have as medium propanol.

## 4. Conclusions

Nanocrystallite samples of  $Ce_{1-x}Zr_xO_2$  were successfully synthesized under supercritical conditions via solvothermal method.

For the effect of solvent in pure and doped ceria, two solvents were studied, propanol and distilled water. It was noticeable for both cases that when the solvent is propanol the particles produced are smaller. For the case of the pure ceria, smaller clusters were also formed when propanol was used.

The effect of composition was studied in distilled water with compositions of 100%, 75%, 50%, 25% and 0% of cerium. First of all, it was possible to conclude that the percentage of cerium expected and the one obtained were slightly different, being the

experimental bigger than the theoretical value, presumably because of the solubility of the zirconium precursor in water. Also, the quantity of cerium has little influence on the crystallite size and average size of the particle. However, the size of the clusters

decrease with the increase of zirconium. In addition, the crystallite size and the particle average size is similar indicating that the sample is composed of monocrystals. In relation to the specific surface area, a disparity of values was noted ranging from 130 m<sup>2</sup>/g to 230 m<sup>2</sup>/g. It was not determined a relation between the specific surface area and the quantity of cerium. It is noteworthy that just one analysis was made per sample so this values can be slightly different when repeated the analysis.

The effect of the residence time of a mixture of 50% of cerium was studied in distilled water. An increase of the crystallite size is observable when the residence time increases. This result was expected due to the fact that the more time the particle is inside of the reactor more it grows.

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