

# Nanoparticles of Co promoted with Ce and Sr in Carbon Nanotube Structures for Tri-reform

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## Introduction

Tri-reforming of methane has the potential advantages of combining all the three reforming processes in a single reformer unit by utilizing flue gases to reform the natural gas to produce syngas. Optimizing the flue gas composition by a pre-processing unit, syngas with the desired CO/H<sub>2</sub> ratio can be obtained with less carbon deposition as well as less energy requirements. A major limitation of methane reforming processes is the rapid deactivation of the catalyst, which has commonly been attributed to the sintering of the active sites of catalyst and carbon formation on these sites, induced by methane decomposition and CO disproportionation or Boudouard reaction.

Nanostructured systems are of great interest, both from a fundamental science perspective as technological applications. Currently, in general, any material that contains grain clusters, plates or filaments dimensions below 10 nm may be considered as nanostructured, as long as their properties differ from those of the extended solid. Such materials have been extensively studied in recent years because the small size of its primary building units (whether particles, grains or phases) and high surface/volume ratio resulting in mechanical, optical, electronic and magnetic individuals.

The goal of the project is to synthesize nanostructured materials, carbon nanotubes (CNTs) modified with metals, characterize them as the structure and morphology and apply them in the process of tri-reforming of methane to produce syngas. It is intended to test these new catalysts in the reaction, aimed at selectivity of products and conversion of methane. The system will be tested for catalytic units and characterized by different techniques.

## Materials and Methods

For the synthesis of the catalyst 5%Co7%Ce3%Sr/MWCNT was used the method proposed by Astinchap et al., 2012 [1]. The first step was to prepare the solutions of the metals impregnation. The second step was to fill the cavity of the nanotube solution with the precursor metal. Initially, it was added to the carbon nanotubes, cerium and strontium solutions at room temperature. The filling of nanotubes occurs by capillary action only at the tips. To the solution entered the carbon nanotube, it was necessary to create a vacuum and to restore atmospheric pressure several times so that the pressure difference inside and outside induces the penetration of the solution into the cavity of the nanotubes. After this step, a treatment with ultrasound was applied for a few minutes to obtain a better dispersion of the nanotubes in solution. Then the mixture was lyophilized and then, at this stage, we have taken the sample solution [Ce-Sr] inside and outside MWCNTs. The third step of the synthesis consisted in washing the outer wall of the nanotube. First it was added to the solution an amount of 10 ml of benzene, protecting the particles within the next wash as benzene does not dissolve the [Ce-Sr] salt and penetrates through the open ends of the capillary nanotubes. The excess benzene was removed

and shortly thereafter, the solution was washed with deionized water, which is immiscible with benzene and is capable of dissolving the [Ce-Sr] present in the outer wall. This step of washing with water was carried out. After this step was again performed lyophilization to obtain well-separated MWCNTs. At this stage, we carbon nanotubes filled with the Ce-Sr salts only in internal cavities. The fourth step was the reduction of [Ce-Sr] salt in a league in CeSr fcc phase, which heated the material [Ce-Sr]@MWCNTs 600°C under 5°C/min for 5h under an atmosphere of 5% H<sub>2</sub> in argon.

## Results and Discussion

In this section are presented the results some characterizations of the functionalized nanotubes.

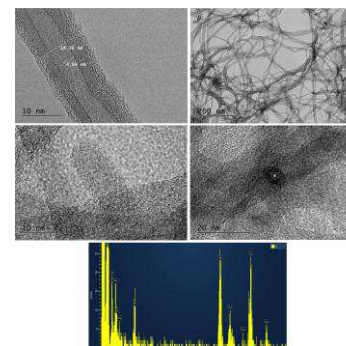
### 1. Nitrogen physisorption

The value of the specific surface area (S<sub>g</sub>) of commercial functionalized carbon nanotubes with carboxylic acid (MWNTC<sub>acc</sub>) was 306.2 m<sup>2</sup>/g. The sample presented a value of greater specific area than presented by multi-walled carbon nanotubes (150 to 300 m<sup>2</sup>/g) [2] due to the attack that the functionalizing agents promoted on the walls of the nanotubes.

### 2. Transmission electron microscopy (TEM)

The transmission electron microscopy images, and enables the identification of the filamentous form of carbon present in the sample, enable achievement of internal and external diameter measurements, number of walls and spacing interlayer. Figure 1 presents a micrograph of the carbon nanotube functionalized with carboxylic acid.

**Figure 1.** Image Transmission Electron Microscopy (TEM) of carbon nanotube functionalized with carboxylic acid.



## References

1. Astinchap, B., Moradian, R., Ardu, A., Cannas, C., Varvaro, G., and Capobianchi, A. *Chem. Mater.* 24, (2012).
2. Serp, P. in: Serp, P., Figueiredo, J. L., "Carbon materials for catalysis", 1 ed., 9, New Jersey, USA, John Wiley & Sons.