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MULTIPLE-WALL CARBON NANOTUBES OBTAINED WITH MESOPOROUS MATERIAL DECORATED WITH CERIA-ZIRCONIA

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ABSTRACT

In this work, Ceria-Zirconia on ordered Santa Barbara mesoporous silica (Ce-Zr-SBA-15), has been used directly as a catalyst for the synthesis of carbon nanotubes (CNTs) through Chemical Vapor Deposition (CVD). In addition to cerium oxide, it contains zirconium oxide nano crystallites, which act as catalysts for carbon nanostructures. The catalytic performance of this material was evaluated for the decomposition of ethanol at 900 °C, with N_2 flow. The carbon decomposed from absolute ethanol diffuses through the surface of the nanostructured catalytic material and precipitates in the form of MWCNT structures, which could be identified by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), showing average diameters of 30-35 nm.

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1. INTRODUCTION

In the past two decades, carbon nanotubes (CNTs) have been the target of extensive research due to their uniqueness and incomparable physicochemical properties, and their possible applications in nanoscience and nanotechnology. Examples include electronics, high-strength polymer compounds, water-gas shift and production of H_2 [1-3]. This technological relevance gave rise to intensive research activity on catalytic chemical vapor deposition (CVD), which has been widely considered for the large-scale synthesis of CNT of the decomposition of various hydrocarbons using transition metals as catalysts in different metals and oxide supports [4]. Unfortunately, large-scale production of CNT through catalytic CVD is still expensive. In addition to the availability of the source of C, the main cost factors are derived from the preparation of substrates, and the finely dispersed diffusion of metallic particles (Fe, Ni or Mg) on them. Zirconium oxide has weak acidic and basic centers that favor selectivity to the desired product, as well as being stable in oxidizing and reducing atmospheres. The cerium oxide exhibits catalytic activity in the coupling of carbon-carbon bonds in aldol condensation reactions. Some characteristics of the surface that influence the catalytic activity of this material are related to the redox properties of the surface, the oxidation state and the coordination of the surface atoms. Cerium and zirconium oxide catalysts exhibit acidic and basic properties that can be used in organic reactions. There are no previous data on the use of these oxides combined and supported on a mesoporous material to obtain CNT. The main objective of this work is the development of MWCNT using Ce-Zr-SBA-15 as a catalyst

2. EXPERIMENTAL

The synthesis of the ordered mesoporous silica SBA-15 was made according to previous work [5] and its description can be found in the **Supplementary Material (SM), Appendix A1**. Ceria and zirconia were incorporated into the Si-SBA-15 support by the wet co-impregnation method for the bimetal catalyst. The catalyst is called Ce-Zr-SBA-15. The synthesis of carbon tubes was carried out by the Chemical Vapor Deposition (CVD) technique using a carbon source (ethanol), vaporizing it or introducing it into a transport gas, so that it came into contact with the Ce-Zr-SBA-

15 catalyst. The working temperature was 900 °C; a quartz reactor of 10 mm for 600 mm was used, with a reaction time of 30 min. The equipment used for characterization is described in **(SM, Appendix A1).**

3. RESULTS AND DISCUSSION

Figure 1(a) shows the Nitrogen isotherm and (b) low-angle XRD pattern. The sample has a typical type IV isotherm with H1 type hysteresis cycle, typical of the SOP-15 mesoporous structure. When ceria and zirconia are incorporated, the hysteresis cycle is briefly altered, presenting a relative pressure range (P / Po) of 0.4–0.8, as shown in Fig. 1(a), while SBA-15 is generally seen in the P/Po region of 0.6-0.8. This suggests some irregularities in the porous system that could indicate that cerium and zirconium oxides are partially blocking mesopores. The textural properties of Ce-Zr-SBA-15 compared to pure SBA-15 (SM Appendix A2, Fig. A2), indicate that Ce-Zr-SBA-15 has the typical fibrous morphology and long mesochannels (1.0– 1.5 μm) corresponding to SBA-15.

XRD of mesoporous materials as-synthesized SBA-15 support and Ce-Zr-SBA-15 at low angle was obtained **(SM Appendix A3, Fig. A3).**

Figure 1 (b) show three diffraction peaks corresponding to planes (100), (110) and (200) of the ordered 2D p6mm hexagonal pore structure typical of SBA-15 used as a reference. The main peak at 2θ = 0.82-0.87°, (100) plane attributed to the presence of regular intermediate spaces between the walls of the mesoporous channels; the other two additional peaks, long-range ordered pores seem to be preserved in the sample.

Figure 1

The inset figure shows high angle diffraction patterns of Ce-Zr-SBA-15. The crystalline phase of ZrO_2 was not found, suggesting that the Zr species are well dispersed. In contrast, Ceria has crystallites of 6 nm, given by Scherrer's formula [6], not well dispersed in the catalyst. Using XPS (Fig. 2) with an associated error of ± 0.2-0.4 eV, we investigated the interactions between silica oxide and zirconium-cerium oxides in the catalyst. The binding energies of Zr $3d_{5/2}$ and $3d_{3/2}$ and

Ce $3d_{5/2}$ and $3d_{3/2}$ reveal that Zr is in its maximum oxidation state (4+) and Ce in the oxidation states 4+ and 3+. The signal around 183.7 eV is attributed to $ZrSiO_4$, while no isolated ZrO2 was found at 182.5 eV, suggesting that Zr as oxide is within the pores of SBA-15 (the relative abundance of Zr as ZrO_2 63%, $ZrSiO_4$ 37%). Ceria spectra showed two chemical environments that lead to the level of the Ce3d nucleus: one around 886.1 eV and the other around 916.6 eV, attributed to Ce_2O_3 and CeO_2 with a relative abundance of 32.29 and 67.71% respectively in accordance with the literature [7].

Figure 2

The X-ray diffraction pattern of the MWCNT is shown in Fig. 3a. The peak at 25.55° (plane 002) corresponds to the pure graphite structure of the multi-walled CNT. The peaks confirming the appearance of the MWCNT at 43.3° and 55.1° are assigned to planes (101) and (004), respectively. The displacement of plane 002 of SWCNT, the single wall CNT **(SM Appendix 4, Fig. A4),** is a function of the diameter of the CNT [8]. The peak profile can be adjusted with two Voigt spectral functions and by setting the parameters of peak 2 (the strongest component of the 002 plane); the Bragg angle (2θ) increases with respect to the 002 plane of the SWCNT to about 27.5º (d= 3.24Å), with a mean diameter of the MWCNT ≥ 30nm [9].

Fig. 3b shows the Raman spectra of the sample. In this analysis, we observe two peaks, the G peak at approximately 1580 cm^{-1} is associated with the stretching vibrations C = C, this peak originates in the stretching mode of the sp^2 hybridized carbon bond that indicates the existence of carbon of crystalline graphite. The second peak at 1340 cm^{-1}, assigned as peak D, is related to vacancies, amorphous carbon, defects and carbonic impurities (this band shows damage of the graphene sheet), this band is induced by disordered bands. We can evaluate the degree of graphitization through the intensity ratio of the D and G peaks (ID / IG). The peaks were integrated, and the results show that ID / IG is 0.9. Too high a temperature can cause a loss of degree of crystallinity to form amorphous carbon and will also result in self-pyrolysis of ethanol. Furthermore, in the spectra, we can observe a broad peak (2500- 3000 cm^{-1}), which **represents** the characteristic 2D peak of graphitic carbon. The existence of these peaks can be explained by the denatured wall of tubes [10]. The SEM of SBA-15 and Ce-Zr-SBA-15 confirm a fibrous

morphology and large meso channels **(SM, Appendix 6, and Fig. A6)**. It has been shown [11], that a decrease in the flow rate ratio (N2/carbon source) produces a lower amount of CNT. The reaction products containing substantial amounts of disordered CNTs and the additional carbon supply deactivate the surface of the catalyst forming an amorphous carbon layer on it and on the walls of the CNTs. In addition, the high ID/IG ratio would indicate the existence of disordered carbon and impurities. The SEM studies for the CNT, show tubes of different lengths (5-7 μm), and diameters ≥ 30 nm (Fig. 3c), straight and other curved The HRTEM image in Fig. 3d shows the multi-walled carbon nanotube. It can also be clearly observed that the nanotube has a diameter of about 30-35 nm and multiple walls in concordance with the XRD and Raman studies.

Figure 3

Thermogravimetric analysis (TG) performed under air atmosphere, reflects the weight loss of CNT at two temperatures, Ti and T0 (beginning of oxidation process and maximum weight loss) respectively. The thermal combustion of the purified CNT begins at 340 °C reaching high temperatures, with a loss of mass of about 85%. The remaining 15% is due to impurities in the CNT during the synthesis process, including defects in the outer layers of graphite. **(SM, Appendix 5, Fig. A5**). Morphologically, CNTs show a rough surface, and this feature can add more surface activity for bio- and nano-applications. The catalytic nanoparticle can exhibit two different behaviors in the nanotube growth process. "Base growth" (catalyst anchored to the substrate), and "Tip growth" (the particle rises from the substrate and is on top of the CNT). The difference in growth modes is probably related to the adhesion or anchorage forces between the substrate and the catalyst; if the adhesion force is weak, the tip growth mechanism is favored, while a strong interaction causes the base growth. In this work, the first results would indicate that the mechanism of growth is of the type "base growth". Being the first and novel CNT synthesis, we continue to explore the optimization of some synthesis parameters and the purification of the MWCNT, in order to achieve uniformity in its production

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CONCLUSIONS

SBA-15 mesoporous material was synthesized and Ceria-Zirconia was introduced by wet impregnation. Different characterization techniques revealed that there were no significant changes in the support, obtaining the catalyst Ce-Zr-SBA-15. We have demonstrated that by using ethanol as a carbon source, through CVD in the Ce-Zr-SBA-15 catalyst, multi-walled carbon nanotubes of approximately 30-35 nm diameter can be successfully obtained. Raman analysis revealed that the materials have a high ID/GI, which indicates the existence of disordered carbon and impurities. XRD, Raman, as well as HRTEM studies indicated the formation of MWCNT, while SEM microscopy exhibited straight and curved carbon nanotubes.

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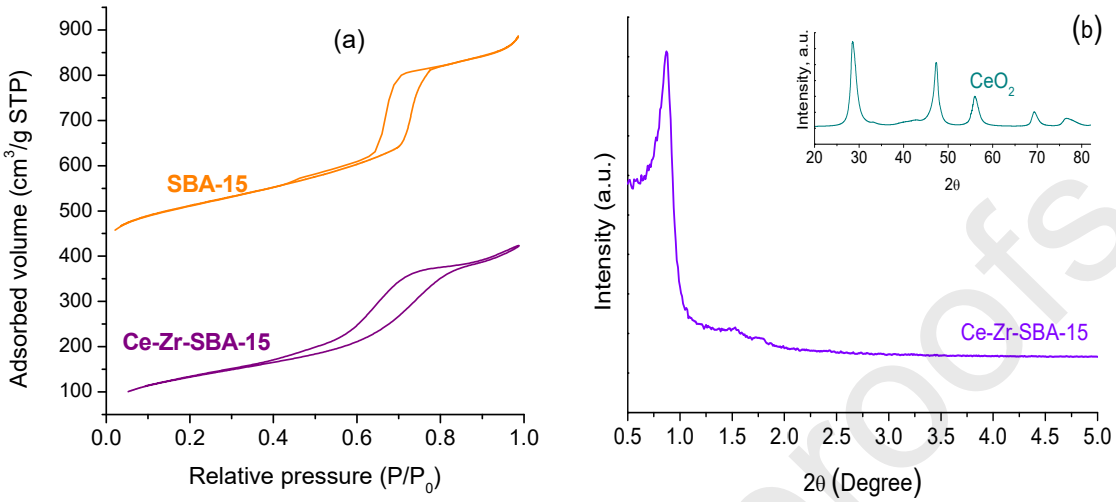


Figure 1. SBA-15 and Ce-Zr-SBA-15: (a) N2 isotherm, (b) XRD at low angle, inset XRD at high angle of Ce-Zr-SBA-15

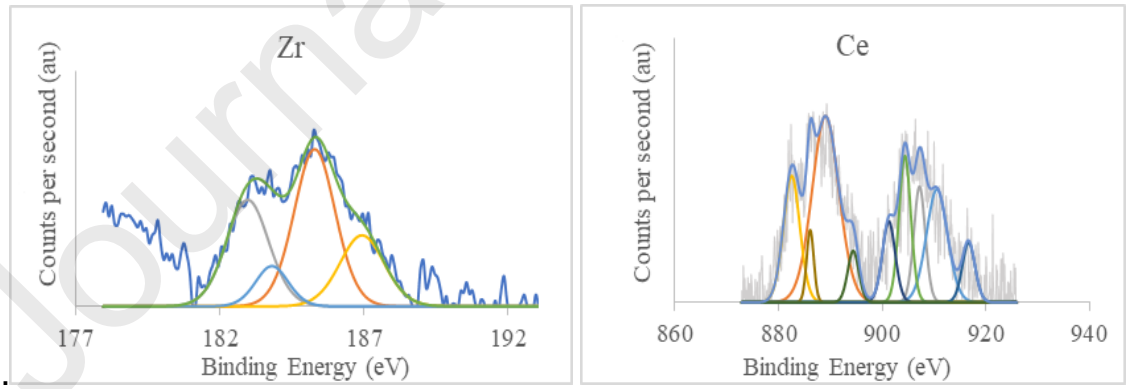


Figure 2: XPS for Zr and Ce species in Ce-Zr-SBA-15 catalyst

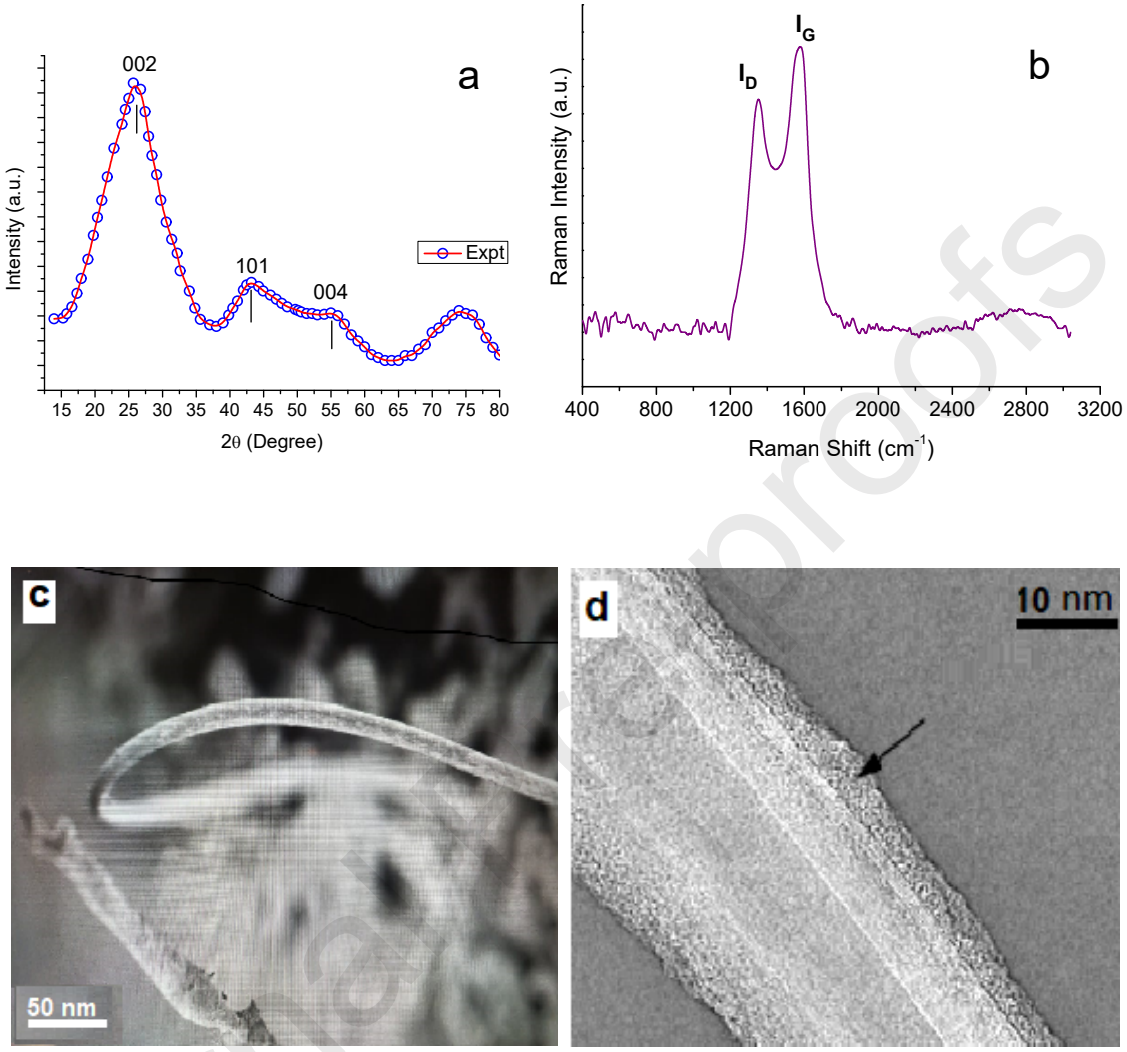


Figure 3: XRD (a), Raman (b), and SEM (c) and HRTEM (d) images of MWCNT

Credit Author Statement

Miguel Rodriguez: Methodology, Investigation

Oscar A. Anunziata: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing.

Andrea R. Beltramone: Conceptualization, Methodology, Investigation

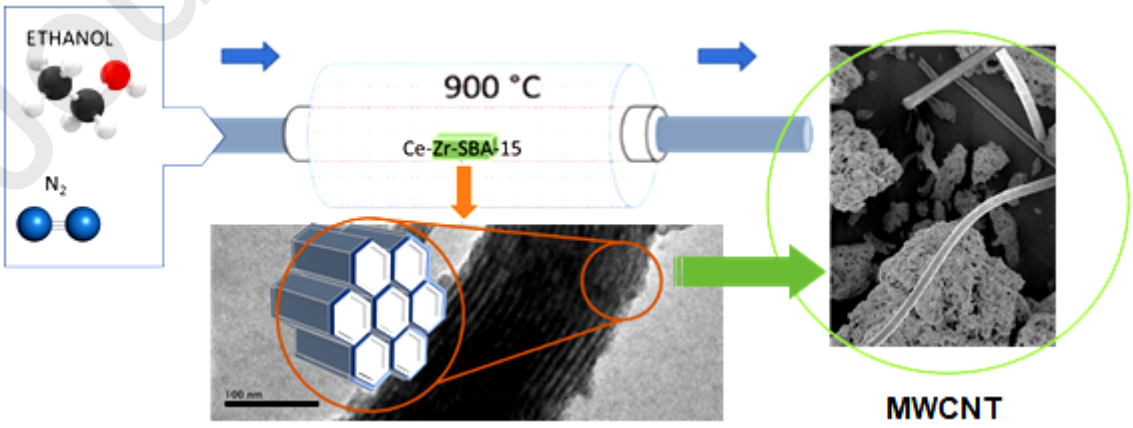
Maria L. Martinez: Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - **review & editing, Supervision.**

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

GRAPHICAL ABSTRACT



* N

* C

* Zr is found as +4 and Ce shows different occupations of level 3d in its final state on the catalyst

* Efficient chemical vapor deposition of ethanol on mesoporous catalyst Ce-Zr-SBA-15

* The prepared multi-walled carbon nanotubes range from 30 to 35 nm in diameter