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# Nucleation and growth of $Ni^0$ nanoparticles and thin films by TEM electron irradiation

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ABSTRACT

This paper reports the *generation in situ* of $Ni^0$ nanoparticles and thin films by focusing a TEM electron beam over $NiO/ZrO_2$-$CeO_2$ and NiO. Electron irradiation was carried out using a TEM at 80 and 100 kV, concentrated over individual $NiO/ZrO_2$-$CeO_2$ and NiO agglomerates. The results showed that just after electron irradiation started, the reduction of NiO phase occurred and fine $Ni^0$ nanoparticles were formed. These Ni nanoparticles were limited to a small area around the irradiated $NiO/ZrO_2$-$CeO_2$ and NiO agglomerates. It was found that the nanoparticles growth increased with irradiation time, and a $Ni^0$ thin film was formed after 50 min. The evolution was studied using BF images and SAD patterns. Characterization of single nanoparticles was conducted using HRTEM, STEM and EDS.



## 1. Introduction

Much efforts have been devoted to the study of the synthesis of metal nanoparticles due to many applications in nanotechnology. The metal nanoparticles are used in conservation of works of art, information storage, gas sensors, fuel cell, rechargeable batteries, biomedical and catalysis applications, among others [1,2]. On the other hand, recent advances in transmission electron microscopy (TEM) have enabled new insights into the structural properties of metal nanoparticles, because it gives physicochemical information at nanometer and subnanometer level. However, it is a fact that, any material observed in a TEM is bombarded with high energy electrons leading to the rupture of chemical bonds [3], provoking important changes at nanostructural level, and hence modifying its local physicochemical properties (for example, chemical reduction by loss of oxygen) [4]. Electron-beam could generate amorphous regions or the transformation of one crystalline phase to another [4].

There are several phenomena reported on the modification of a sample during the electron-irradiation in a TEM. One of the most known is the electron beam-induced fragmentation (EBIF), this is a term used to describe the phenomenon in which nanocrystals are formed by irradiating a large material with a high energy electron beam. The larger particles of the source material shrink and simultaneously it is fragmented, forming a field of smaller nanocrystals around it, generally of the same phase or of similar composition. EBIF has been reported for several authors, Ru [5] proposed that the fragmentation observed in Au particles was primarily the result of a combination of thermal and electrical effects induced by the electron beam, which was further enabled by the presence of excess at vacancies and voids in the micrometer-sized parent particles. Other materials reported with EBIF phenomenon are Pb [6], $SnO_2$ [7], GeTe [8], BiNi [9,10]. Recently, Caldwell et al. [11] have investigated the generality of EBIF of a wide variety of materials and showed that EBIF occurs by a mechanism in which the materials go through a thermally induced phase transition, like it was proposed initially [5].

Another different phenomenon was reported by Sepulveda-Guzman et al. [12], they found that metallic Bi nanoparticles were formed after 30 min by electron-stimulated reduction of sodium bismuthate. The $Bi^0$ nanoparticles were formed over the irradiated agglomerates and they were not ejected out the agglomerate, showing a difference with EBIF. On the other hand, Ming-Yu et al. [13] reported the Cu isolated nanoparticles formation by *in situ* TEM irradiation. Evolution of Cu nanoparticles from the synthesized CuCl was observed from the position with apparent incomplete encapsulation. The effect of polymer encapsulation, acting as a soft template, was important to influence the nanostructure growth. Another interesting paper was reported by Wang et al. [14], they proposed a growth mechanism of Cu nanorods on carbon films by manipulating electron irradiation on a Cu powder. Others methods to produce metallic nanoparticles *in situ* in a TEM have been

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reported [15–18]. All these authors reported the formation of nanoparticles over the precursor material as a consequence of the irradiation process. In some cases, they used controlled heating, reducing agent or template.

One aspect that has not been reported so far is the process of formation of nanoparticles around the material irradiated, and subsequently, the slow formation of a thin film as a consequence of continuous electron beam irradiation. Therefore, this paper reports the nucleation and growth of $Ni^0$ nanoparticles by electron-irradiation of $NiO/ZrO_2$-$CeO_2$ and NiO agglomerates, followed by the detachment of small-sized Ni particles and likely Ni adatoms that move from the agglomerates surfaces and redistributed radially over carbon surface to finally coalesce and form a $Ni^0$ thin film.

## 2. Materials and methods

### 2.1. $NiO/ZrO_2$-$CeO_2$ system

The $NiO/ZrO_2$-$CeO_2$ catalyst was synthesized by the sol-gel method, from $Ni(NO_3)_2{\cdot}6H_2O$, $Ce(NO_3){\cdot}6H_2O$, $Zr(OBu)_4$ (80 wt.%) and $HNO_3$ (Aldrich), as it was reported [19]. The amount of each reactive was calculated in order to obtain 10 g of catalyst. The Ni content was 15 wt.% and the $CeO_2$ concentration was 20 wt.%. The preparation procedure was the following: a proper amount of $Zr(OBu)_4$ was dissolved in 700 ml of isopropyl alcohol (to form a 2 wt.% $ZrO_2$ solution) and stirred for 2 h. The hydrolysis of the alkoxide solution was carried out at 5 °C, adding drop wise a solution of $H_2O$ ($H_2O/Zr(OBu)_4$ = 4 molar ratio), $Ni(NO_3)_2{\cdot}6H2O$, $Ce(NO_3){\cdot}6H_2O$, $HNO_3$ ($HNO_3/Zr(OBu)_4$ = 0.2 molar ratio) and 100 ml of isopropyl alcohol. The green rigid transparent gels obtained were aged *in situ* for 24 h and then dried in air flow at room temperature. The dry gel was carefully calcined in air at 500 °C during 2 h with a 100 Nml/min flow. The calcined solid was crushed, sieved and the fraction with a 0.16–0.40 mm particle size separately for analyze, and then was heated at 10 °C/min and calcined in air at 800 °C during 6 h with 50 ml air/min. Finally, the sample was evaluated catalytically in methane reforming with $CO_2$ [19].

### 2.2. Unsupported NiO system

The NiO system was prepared from a solution of nickel nitrate, $Ni(NO_3)_2{\cdot}6H_2O$. To 0.5 mol of the green solution, ammonium hydroxide ($NH_4OH$) was added until the solution turns blue and the precipitation of a solid component becomes evident. The suspension formed is then heated to 80 °C, at constant stirring rate. The suspension was removed from heating when all liquid had evaporated. The solid fraction was heated at 500 °C for 2 h in the oven before X-ray diffraction analysis.

### 2.3. Irradiation experiments

$NiO/ZrO_2$-$CeO_2$ catalyst was powdered and dispersed in ethanol, and then loaded over the copper grid with carbon continuous film. The grid was dried before TEM analysis. The electron irradiation experiments were performed inside the chamber of a TEM JEOL JEM 100CX with tungsten filament. The accelerating voltage and the vacuum chamber were set to 100 kV and $1.33 \times 10^{-4}$ Pa, respectively, by focusing the beam with the condenser lens, to the crossover point, until the minimal diameter was reached. The beam diameter was *ca.* 6 μm and the current density *ca.* 100 pA/cm$^2$. The irradiation experiment evolution consisted of taking images at different times. In addition, a series of irradiation experiments were performed in the NiO system, following a similar procedure that $NiO/ZrO_2$-$CeO_2$ sample. The effect of the electron energy of the beam was evaluated by modifying the accelerating voltage, *i.e.*, from 20 kV to 100 kV.

### 2.4. Characterization

The irradiation effects were followed by expanding the electron beam of a JEOL JEM 100CX microscope. The evolution of the nanoparticles growth was observed through both, Bright Field (BF) imaging and Selected Area Electron Diffraction (SAD) patterns in the same instrument. After the sample was irradiated inside the chamber of JEOL JEM 100CX microscope, the TEM grid was taken out and put in a field emission Scanning and Transmission Electron Microscope (STEM) JEOL JEM2200FS. High Resolution Transmission Electron Microscopy (HRTEM), Energy Dispersive X-Ray Spectroscopy (EDS) and elemental mapping analysis, were conducted in the same microscope in order to analyze single nanoparticles. HRTEM digital images were obtained using a CCD camera and Digital Micrograph Software from GATAN.

## 3. Results and discussion

### 3.1. $NiO/ZrO_2$-$CeO_2$ system

I*n situ* formation of $Ni^0$ nanoparticles through electron beam irradiation has been performed using a TEM. Isolated $NiO/ZrO_2$-$CeO_2$ agglomerates of several microns were irradiated, as described in Section 2.3, and only a few seconds after starting the irradiation process a lot of nanoparticles were ejected over the carbon support (image not shown at first seconds, but the irradiated agglomerate correspond to zone A of Fig. 1a).

At 10 min of electron irradiation over the zone A (Fig. 1a), nanoparticles were radially spread out from the agglomerate target and the nanoparticles presented a ≤45 nm average size. The average size decrease with distance to the irradiated agglomerate marked as A (from right to left on the micrograph). The upper histogram was built in order to quantify the nanoparticle size with distance, it becomes evident the relation between distance and beam irradiation intensity. The electron beam was expanded (in this conditions nanoparticles are not formed) and a SAD pattern was obtained (Fig. 1b). At 10 min of continuous irradiation, rings with scarce reflections were identified as FCC lattice with Fm-3 m space group, 0.35238 nm of cell parameter, and interplanar distances measured matching to metallic Ni (PDF database file 4-850) become evident. The diffraction pattern was indexed as (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections, indicating an incipient polycrystalline nature. It is important to notice that (2 0 0), (2 2 0) and (3 1 1) reflections are not well defined which suggest that the nanoparticles are formed in small diffraction domains. However, the diffraction rings also showed small bright spots arguably become the presence of considerable well defined crystals. The diffuse ring between (2 2 0) and (3 1 1) reflections corresponds to the amorphous carbon support from the grid.

The electron beam was expanded every 10 min up to reach 50 min. During this irradiation process, the nanoparticles formed grew by a coalescence mechanism, where nanoparticles moved over the carbon support until covering it completely. At 50 min (Fig. 2a), the film formed resembles previously reported thin film of gold, obtained after the evaporating process in order to prepare a TEM standard with Au [3]. The SAD pattern (Fig. 2b) shows well-formed continuous rings, characteristic of a polycrystalline structure. The diffraction pattern was identified as FCC lattice. According to the PDF database the diffraction pattern matches with metallic Ni (PDF database file 4-850). Reflections were indexed as (1 1 1), (2 0 0), (2 2 0) and (3 1 1). The reflections were perfectly