

Synthesis of the Mg₂Ni Alloy Prepared by Mechanical Alloying Using a High Energy Ball Mill

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Abstract. Mg₂Ni was synthesized by a solid state reaction from the constituent elemental powder mixtures via mechanical alloying. The mixture was ball milled for 10 h at room temperature in an argon atmosphere. The high energy ball mill used here was fabricated at ININ. A hardened steel vial and three steel balls of 12.7 mm in diameter were used for milling. The ball to powder weight ratio was 10:1. A small amount of powder was removed at regular intervals to monitor the structural changes. All the steps were performed in a little lucite glove box under argon gas, this glove box was also constructed in our Institute. The structural evolution during milling was characterized by X-ray diffraction and scanning electron microscopy techniques. The hydrogen reaction was carried out in a micro-reactor under controlled conditions of pressure and temperature. The hydrogen storage properties of mechanically milled powders were evaluated by using a TGA system. Although homogeneous refining and alloying take place efficiently by repeated forging, the process time can be reduced to one fiftieth of the time necessary for conventional mechanical milling and attrition.

Keywords: Mechanical Alloying, Mg₂Ni alloy, Hydrogen Storage, X Ray Diffraction, Scanning Electron Microscopy.

Introduction

Over the years several countries have defined uses for hydrogen storage because of the rising demand for traditional fuel and the associated problem of global warming caused by CO₂ emissions. Hydrogen has come into the world's spotlight as a potential clean and high capacity energy source. Hydrogen storage is an important issue for hydrogen economy development. The aim of this technological challenge is to store the maximum amount of gas in a minimum of volume or mass of storage system safety. Nowadays the most popular storage method is based on compressed hydrogen gas. High pressure storage gas is performed by Type III or IV Tanks [1].

The major challenges related to materials for hydrogen storage can be summarized by gravimetric hydrogen density. Since very few hydrogen storage materials reach a metal/hydrogen ratio higher than 2, hydrogen storage materials fulfilling international goals should be based on light weight elements. Thermodynamics: The release of hydrogen should take place at conditions (temperature and pressure) matching working conditions, for example for fuel cells. Reversibility: Important for onboard storage, but for offboard hydrogen regenerative hydrogen storage materials the hydrogen uptake should be a cheap and simple process. Kinetics: The use of catalysts, is often important, but also the use of nano-scale

Resumen. El intermetalico Mg₂Ni se sintetizó a partir de sus elementos básicos mediante aleado mecánico. La mezcla de elementos se molió durante 10 horas a baja temperatura y en atmósfera de argón. El molino de aleado mecánico de alta energía utilizado en la preparación de la aleación fue diseñado y construido en el ININ. Se mantuvo una relación de peso de los medios de molienda/intermetalico de 10:1. Estos materiales se colocaron en un contenedor de acero inoxidable y tres medios de molienda de 12.7 mm de diámetro. La preparación del compuesto Mg₂Ni se realizó en una pequeña caja de guantes hecha de lucita y también fue construida en nuestro Instituto para evitar la presencia de oxígeno. La evolución del intermetalico durante el tiempo de molienda se caracterizó por difracción de rayos X y microscopía electrónica de barrido. La reacción de hidrogenación se llevo a cabo en un micro-reactor controlando presión y temperatura, la cantidad de hidrógeno en el intermetalico se evaluó mediante análisis termogravimétrico.

Palabras clave: Aleado mecánico, intermetalico Mg₂Ni, almacenamiento de hidrógeno, difracción de rayos X, microscopía electrónica de barrido.

materials will improve kinetics. In addition, several other factors are of importance such as the availability of elements and compounds, cost issues and safety [2]. Different classes of materials for hydrogen storage have been intensively studied during the last decades. Diverse methods exist to prepare metallic alloys between them is the mechanical alloying technique. This process presents certain advantages e.g. smaller restrictions with respect to composition - nanocrystalline, amorphous, quasicrystals phases can be obtained. The intermetallics in form of powders and low temperatures can be prepared [3]. Although the technique has been used quite extensively, at present the process of mechanical alloying is not completely understood. It is suggested that the alloy generated due to the collision of the balls resulting in continuous fragmentation, coalescence events of the alloy at the collision sites are the steps of the process of mechanical alloying. Research and development of hydrogen storage materials has shown that, instead of AB₅ type alloys such as LaNi₅ or CaNi₅, more powerful and light A₂B type alloys have played an important role [4-6]. Among them, Mg₂Ni is one of the most promising hydrogen storage alloys forming the Mg₂NiH₄ hydride corresponding to a hydrogen content higher than 3 wt%. Even though magnesium and magnesium alloys are attractive light weight hydrogen absorbing materials, their hydrogen storage properties must be improved for practical applications. The

improvement in their hydriding/dehydriding kinetics is especially important. Some studies have shown that by combining multiphase magnesium with transition metals and intermetallic compounds, its hydrogenation kinetics could be improved. However, the crystal lattice modification of nanocrystalline structures with amorphous phases is also considered an effective method for improving the kinetic properties of the Mg and Mg alloys as well as for dealing with other problems related to those metals [7-10]. In the present paper, the MgNi based alloy was prepared by a spex type high energy ball mill system that was constructed at ININ [11]; the mixture was characterized at different milling time by using X ray diffraction and scanning electron microscopy techniques.

Results and discussion

In the present process of ball milling the Mg₂Ni alloy synthesis was obtained. The evolution of the intermetallic formation was analyzed by X ray diffraction patterns as a function of milling time milled under argon atmosphere every two hours. Figure 1 shows a series of diffractograms indicating the transformation of the compound Mg₂Ni. The first X ray diffractogram (a) corresponds to the sample after 2 hours of milling, which did not undergo any structural change and the main reflections with no variation for the original elements: nickel (100, 002, 101 planes) and magnesium (111, 200, 220 planes) were identified. The Mg₂Ni phase began to form after 4 h of milling time, (Figure 1b) as indicated by the presence of an intensity near 20° (003, 101) and also near 40° (112, 200 planes) characteristic of this phase. On the spectrum, maxima of diffraction of the original elements are even observed. The analysis of these results revealed that the peaks corresponding to magnesium almost disappeared and those of nickel decreased in intensity (111, 200 and 220 planes) and broadened (increased full width at half-maximum (FWHM)). During the process of mechanical alloying, two types of events are carried out during the formation of the alloys: welding and fracture. In the process, the

powders can be caught either between a pair of balls in motion or between a ball and the wall of the vial. The mixture of magnesium and nickel undergo an intense plastic deformation, by which particles in the form of flakes come about, such as is indicated in (Figure 2) after 4 h of milling. These features suggest the beginning of the diffusion of magnesium into nickel which leads to alloy formation.

Figure 1c shows the diffractogram corresponding to the Mg-Ni compound after 6 hours of milling; in this time the main Mg₂Ni phase with diffraction angles near 20, 40 and 45° in 2θ were observed with greater clarity than in both previous spectra (Figures 1(a) and 1(b) respectively); however, the Mg and Ni phases were still present at low concentration without reactive. The MgNi₃C_{0.75} and Mg_{0.4}Ni_{0.6}O phases could not be observed in the XRD patterns during the ball milling process for less than this milling time.

Figure 1d shows the formation of the Mg₂Ni phase after 8 hours of milling, as they show the main maxima of diffraction angles. It can be observed that the elements of Mg and Ni reacted almost completely, and only residues without reacting were detected at this milling time. Finally, the intermetallic of Mg₂Ni was obtained after 10 h of milling whose diffractogram is shown in Figure 1e. No great difference in spectrum of the Figure 1d was observed. However, a new phase originated by the contamination during the mechanical alloying process was identified; this phase was probably caused by the presence of the methanol which was used as a control agent during the milling process. It could be assumed that during the milling process and the high energy impact produced with the milling means, the methanol was dissociated into its component hydrogen, oxygen and carbon. The last two elements could react *in situ* with Mg and Ni compound and the MgNi₃C_{0.75} and Mg_{0.4}Ni_{0.6}O oxide phases were formed. Almost all deflections appear at relatively small angles; the majority of peaks appear overlapped in the different intervals from angles 20.

The Mg₂Ni alloy was obtained with milling times of 8 and 10 h, and the time used in this preparation was very low compared with that reported in the literature [12] and which,

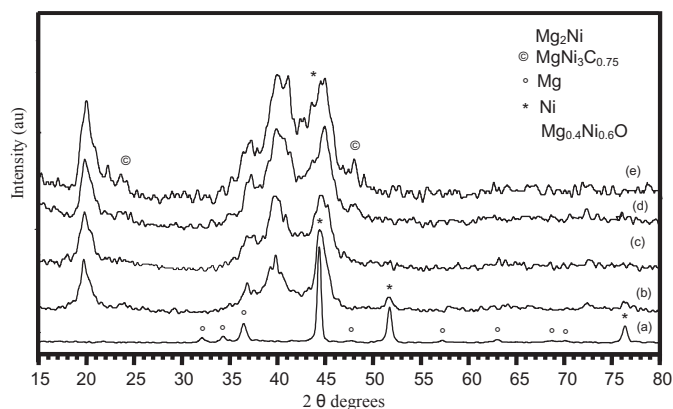


Fig. 1. XRD patterns of Mg₂Ni alloy prepared by mechanical alloying after 2, 4, 6, 8 and 10 h of milling process (a, b, c, d, e) respectively.

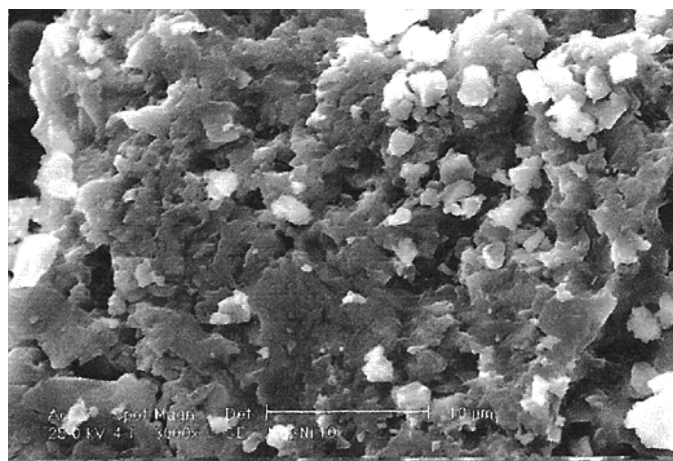


Fig. 2. The SEM micrograph of Mg₂Ni after 4 h of milled.

preparation by the same method of milling time, took 100 hours or more. The Mg_2Ni phase was identified according to the JCPDS (03-056-9375) pattern, and this compound has a hexagonal morphology; thus, other phases were also verified corresponding to the magnesium nickel carbide ($MgNi_3C_{0.75}$) 000280624 pattern with a cubic lattice and magnesium nickel oxide (000340410) pattern with a cubic centered lattice face.

Figure 2 shows the micrograph of the alloy magnesium-nickel after 4 h of mechanical alloying process. A plastic deformation in form of flakes and individual particles that possibly were of magnesium and nickel elements that had not yet reacted by the forces of interaction between milling means were observed. We can notice on the image that after 4 h of milling process the union events and fragmentation were initiated indicating laminar morphology. This phenomenon was observed as well by XRD analysis, as indicated by the presence of intensity in (20.098 and 20.779°) and (37.050 , 39.924° in 2θ angles peaks) characteristic of this phase shown in the X-ray diffractogram pattern (Figure 1b). The synthesis of Mg_2Ni by mechanical alloying process was continued. When two flakes from the atomic point of view are superposed face to face, then the union event also known as “fusion in cold” is produced. The result of repeated events (union and fragmentation) finally produces the microstructural refinement of the material. The competition between the union events and those of fragmentation continue throughout the mechanical alloying process, which is why to obtain a successful alloy a balance between these events is needed.

Figure 3 shows the microstructure of the synthesized Mg_2Ni after ball milling duration, in this case corresponding to 10 h. The particle size of the material was analyzed by SEM. Since no segregation of elements was observed locally, almost

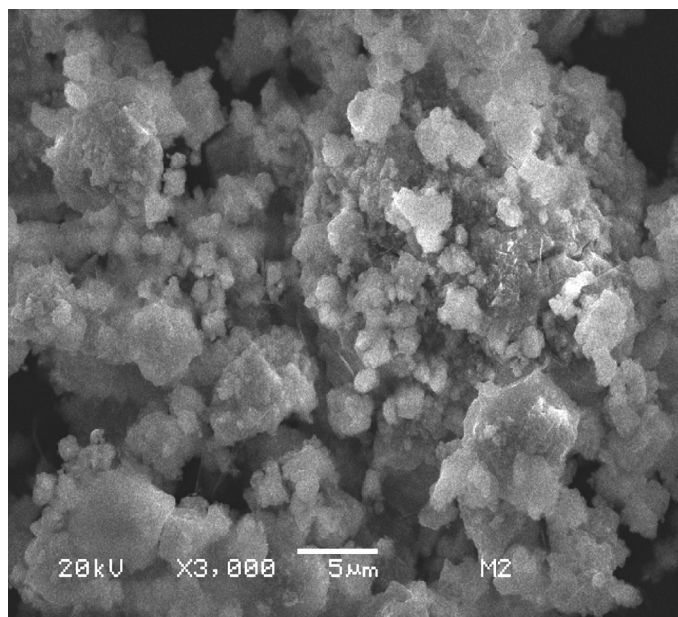


Fig. 3. Micrograph of Mg_2Ni alloy prepared by mechanical alloying after 10 h of milling process.

100% of the initial element mixtures had reacted to form the Mg_2Ni compound. The results of the EDS microanalysis of magnesium and nickel intermetallic powders in the relation (Mg_2Ni) for milling times (2, 4, 6, and 8 h) are presented in Table 1. The values for 10 h of milling process are not indicated because are similar that to 8 h. Methanol was used as control media in these milling processes. The elements reported were: C, O, Mg and Ni. No other element was detected, mainly the Fe, perhaps a small contamination of this element was originated as impurity, but the amount is not sufficient to be detected by the methods used into its characterization. Carbon presence is probably due to the graphite strip used in the sample holder and the characteristic X-rays produced by excitation from the electron beam, and methanol used as control media that was dissociated in its components. Oxygen was not completely eliminated when preparing the sample due also to the presence of control medium (methanol) and air upon manipulating the container. In the same milling process, oxygen reacted with the small amount of magnesium in such a way that the diffraction analysis did not detect the magnesium oxide (MgO). Therefore, the presence of oxygen was not completely eliminated despite the use of the glove box. Figure 4 shows the X-ray spectrum of the Mg_2Ni alloy, the results were obtained by the EDS sound coupled to the scanning electron microscope, the X-ray energy is characteristic of each element that forms the alloy of Mg_2Ni . In the figure the intensities of

Table 1. Result of the microanalysis (EDS) of Mg and Ni milled 2, 4, 6 and 8 hours, with a high energy mechanical alloying system.

Elements	2 h		4 h		6 h		8 h	
	Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %
C	4.24	11.09	3.19	9.27	3.46	9.92	4.06	11.62
O	3.80	7.45	3.22	7.04	3.09	6.67	3.49	7.51
Mg	42.68	55.11	33.31	47.84	34.37	48.73	32.20	45.56
Ni	49.28	26.35	60.28	35.85	59.08	34.68	60.25	35.31
Total	100	100	100	100	100	100	100	100

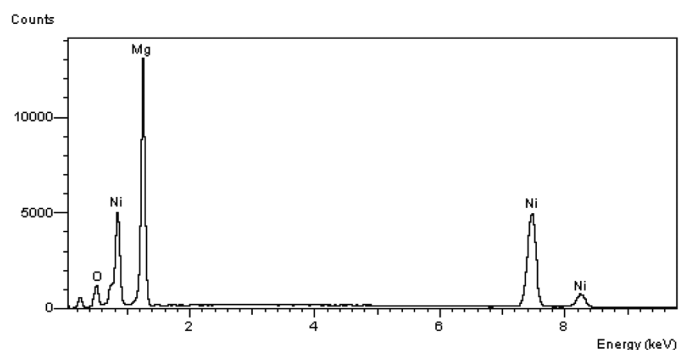


Fig. 4. X-ray spectrum of the Mg_2Ni alloy which was obtained with the EDS sound after 10 h of milling.

C, O, Ni, and Mg were observed. No other element was detected by the EDS analysis. All peaks at low energies are well separated and they are not overlapped. The Fe could be present as impurity from the milling process. This element report X-ray energies of $K_{\alpha 2}$, $K_{\alpha 1}$ and $K_{\beta 1}$ with values of 6.39, 6.40 and 7.06 keV respectively, these energies were not detected during the EDS microanalysis.

These results of EDS were obtained from the all samples types analyzed. The values reported represent the weight and atomic percentage estimate of the elements present in each sample approximately depending of milling time, since the EDS analysis is a semi-quantitative method. The results are found grouped in blocks of columns. The data observed in the columns are of samples milled each 2 h with the same control medium. It can be noted that the stoichiometric relation of the intermetallic has values that are different from those proposed by theories due to the fact that the analysis is carried out in a superficial way and the sample is not found to be uniform; on the other hand, it is known that scanning electron microscopy is not a quantitative technique.

This Mg₂Ni is composed of the powder particles with size from 1 to 3 μm approximately. Keeping in mind that the original powder size was in the order of 200 mesh for both magnesium and Ni elements, this reduction of powder particle size should be attributed to severe plastic deformation/fragmentation events and motion that took place during the present mechanical alloying process. The merit of MA lies in the reduction of processing time duration, because of the design of the mechanical alloyed system. Since the container is longer than other systems used for the same purpose, the normal time duration to prepare Mg₂Ni by mechanical alloying or attrition was estimated to be 100 h or more according to the literature [12, 13]. It should be noted that the present time duration can be further reduced by using the mechanical alloying. The results of the analyses of elemental composition of Mg₂Ni powders after 10 h of milling showed besides magnesium and nickel the presence of oxygen and carbon. The presence of oxygen and carbon is probably due to the methanol used as a control means which prevents that the powders from sticking to the walls of the container as in milling means. With high energy impact the methanol was transformed into hydrogen, oxygen and carbon. These last two elements reacted with Mg₂Ni and the MgNi₃C_{0.75} and Mg_{0.4}Ni_{0.6}O phases in small concentrations were obtained. Therefore, oxidation was able to take place inevitably during the milling process. Sometimes this leads to burning even when handling these reactive fine powders in the presence of a small amount of oxygen in the inert gas atmosphere. Furthermore, since these synthesized Mg₂Ni fine powders are present as coating on the milling balls or the vial walls, it is difficult to collect them after processing, especially for Mg based alloys. This implies the risk of a deterioration of the hydrogen storage capabilities of Mg₂Ni alloys during the long processing duration, being of the order of 10-100 h. These difficulties attributed to contamination are essentially intrinsic to mechanical milling where balls and vials are used for long periods of processing. Through funda-

mental studies, the mechanical reduction of grain size as well as homogeneous distortion of materials result in the formation of fresh intergranular surfaces and at the same time an activation of mechanically induced reactions into nano-sized alloys or amorphous materials. In order to avoid the contamination of intermetallic magnesium-nickel by erosion and the motion of milling means towards the walls of the vial, the milling balls were changed every 2 h; no phase of iron was observed due to the wearing down during the milling process.

To a sample of the intermetallic Mg₂Ni obtained after 10 h of milling, the hydrogenation process was carried out with no previous activation process. Subsequently, the sample of Mg₂Ni-hydride was heated in the TGA equipment for hydrogen quantification. Weight loss vs. temperature graphs was obtained. The first results reported by the thermogravimetric system concerning the effective hydrogen quantity absorbed in this material indicate 2.1% weight approximately under the experimental conditions of mainly pressure and temperature. The Figure 5 shows a thermogram which is representative of hydrogen liberation process from Mg₂Ni. On the spectrum, a first little desorption was produced, which begins at room temperature (18 °C) and ends at 175 °C, Although an additional weight loss is observed to occur at low temperature, it is not taken into account for the total percentage due to adsorbed humidity during sample handling. A second desorption step is observed which start at 175 °C and ends at 325 °C with a maximum H₂ release in this experimental conditions of 2.1%. Stability of Mg₂Ni-hydride sample was confirmed by thermogram obtained immediately after hydrogen absorption preparation for the sample. The thermogram was indicated that, at room temperature, no liberation of H₂ occurs and, that the presence of oxygen (7 At% approximately) does not alter hydrogen content in the alloy. The confirmation that the weight loss during the heating cycle in the TGA system was due exclusively to desorbed hydrogen has been reported elsewhere [14].

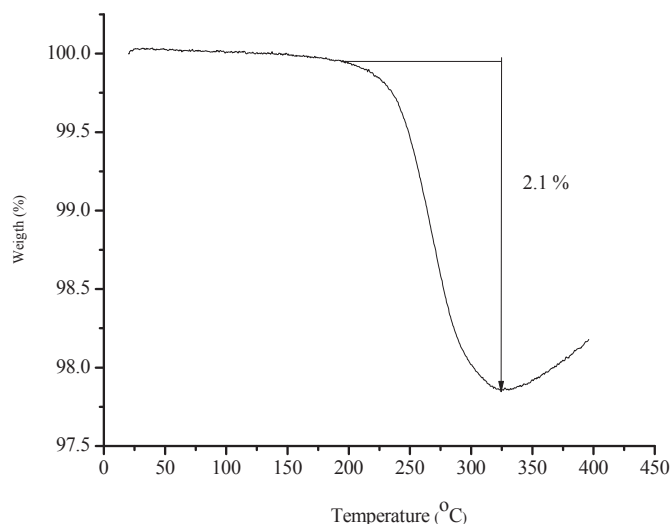


Fig. 5. Thermal analysis of Mg₂Ni alloy after hydrogenation process.

Conclusions

The Mg₂Ni compound was synthesized by a mechanical alloying technique with milling time of 8 to 10 h using a system type spex of high energy which was constructed in the ININ. The ball milling duration in this case corresponding to about 10 h in comparison with that reported in the literature was reduced considerably. It is indicated elsewhere [15] that when the milling time is very long, the situation will deteriorate. For example, after 120 h milling, the material has very poor hydrogen-storage capacity and is difficult to activate. The evolution of the XRD patterns as a function of milling time for Mg₂Ni milled under argon atmosphere was carried out, as shown in Figure 1. The Mg₂Ni phase begins to form after 4 h, as indicated by the presence of intensity in the 20° angle 2θ, characteristic of this phase. The relative intensity of Mg patterns decreases and the peaks broaden drastically. In order to diminish the formation of MgNi₃C_{0.75} and Mg_{0.4}Ni_{0.6}O phases, the control agent (methanol) was reduced to 50%. To avoid contact with the air all samples were handled in an inert atmosphere.

To avoid some contamination by the high energy impact between milling means and the walls of the vial, the milling means were changed every 2 h. In a hydrogenated sample the effective hydrogen capacity of 2.1 wt.% was obtained according to parameters of temperature, hydrogen pressure and reaction time.

Experimental

Elemental magnesium with a purity of 99.8% (200 mesh) and Ni 99.9% (100-200 mesh) were mixed in the desired quantity to reach a nominal composition of 45.3wt% Mg and 54.7wt% Ni corresponding to the stoichiometric mole ratio of Mg₂Ni. The synthesis of Mg₂Ni was carried out by mechanical alloying with a high energy ball mill type spex which was constructed at ININ. Then the Mg and Ni powder were put into a stainless steel vial and three stainless steel balls of 12.7 mm in diameter were used for milling. The ball to powder weight ratio was 10:1. The mixture was ball milled for 10 h, at room temperature in an argon atmosphere. All the alloy samples were handled without exposure to air in a little lucite glove box under argon gas. This glove box was also constructed in our Institute. In order to monitor the possible alloy formation, a small amount of the ball milled material was intermittently taken out from the stainless steel vial at time intervals of 2, 4, 6, 8 and 10 h. From a series of experiments, it was found that these time periods were most appropriate for checking the possible alloy formation. The structural evolution during milling was detected by X-ray diffraction analysis in a diffractometer model Siemens D-5000 adapted to an X-ray tube with a copper anode and used to identify the phases formed. The

measurements were taken at a power of 40 kV, 45 mA. A diffracting beam monochromator and Cu Kα radiation was used. The intermetallic alloy was placed in portable samples with the scanning angular interval from 15 to 80° in 2θ. A Scanning Electron Microscope JEOL 5900 LV equipped with a microanalysis EDS system was used to find the morphology and the chemical composition of the particles. The hydrogenation reactions were carried out in a micro-reactor Parr Instrument model 4842 with a capacity of 50 ml. The sample sorption was achieved according to parameters of temperature, hydrogen pressure and reaction time (200 °C, 10 atm. and 5 min) respectively; the hydrogen used was of ultra-high purity 99.999%. The material was subsequently analyzed by the thermogravimetric method before and after the hydrogenation process with thermoanalyzer equipment TA Instruments model TGA-51, previously calibrated and by programming the heating system from room temperature to 400 °C, employing nitrogen gas as carrier (N₂ high degree purity) at a rate of 10° C/min.

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