**RuNi/MgAl2O4 structured catalyst for CO2 methanation**

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**Abstract**

Novel catalytic systems should be tested for the valorization of CO2 through the Sabatier reaction, since this process is gaining more and more importance within strategic sectors of the chemical industry. Therefore, this work explores the feasibility of structuring a catalyst (0.5%Ru-15%Ni/MgAl2O4) for CO2 methanation using metal micromonoliths. The coating of the catalyst over the surface of the micromonoliths is carried out by means of the washcoating procedure and different characterization techniques such as XRD, H2-TPR, N2-physisorption, Raman spectroscopy and TEM are applied to establish possible changes in the catalyst during structuring.

Regarding the performance in the Sabatier reaction, the structured systems are tested as well as the powder catalyst in order to establish the possible effects of the structuring processes. For this, variables such as the amount of loading catalyst, the space velocity, the inclusion of water in the feed-stream and the pressurization of the process were studied during the catalytic tests.

In general, it can be said that the structuring of the proposed catalyst by the reported procedure is absolutely feasible. There are no substantial changes in the main features of the catalyst and this means that its catalytic performance is not altered after the structuring process either. Furthermore, the structured system exhibits high stability in a long-term test and is comparable with other CO2 methanation catalysts reported in research to date.

**Keywords**

Structured reactors; Ru-Ni catalyst; CO2 hydrogenation; Carbon Capture and Utilization (CCU); Methane production; pressurised CO2 methanation.

1. **Introduction**

The capture and recycling of CO2 is currently a very hot topic, since this can be one of the more suitable ways to decrease the levels of such pollutant in the atmosphere [[1](#_ENREF_1)]. Therefore, the different processes for transforming CO2 into fuels or valuable chemicals have been acquiring special interest. This is the case of CO2 methanation, a hydrogenation process also known as the Sabatier reaction [[2](#_ENREF_2)].

Renewable methane production achieved via Sabatier reaction (Eq. 1) is one of the most interesting power-to-gas (P2G) approaches since this fuel, also known as synthetic natural gas (SNG), may replace natural gas (NG) and it can be directly injected into the already existing distribution grids [[3](#_ENREF_3)]. However, this process is not entirely profitable because it requires very strict thermal control to minimize the manifestation of the Reverse Water-Gas Shift reaction (R-WGS) (Eq. 2) that decreases the methane yield. Furthermore, the supply of hydrogen is another major obstacle to this process [[4](#_ENREF_4)].

(Eq. 1)

(Eq. 2)

In fact, CO2 methanation has long been known and applied at the industrial level, only as a purification step in the production of ammonia, but plants have not been developed solely for this process until the last decade, in which very ambitious goals worldwide to reduce CO2 emissions have been set. For instance, in the Netherlands it is aimed to progressively replace NG by SNG in the near future [[5](#_ENREF_5)]. Additionally, in Germany, which is clearly the current European leader in the promotion of P2G projects, the Volkswagen group launched the Audi e-gas plant, which has been under operation since 2013, and it is based on the direct hydrogenation of CO2 in a single isothermal fixed-bed reactor [[6](#_ENREF_6)]. Nevertheless, although there are more and more initiatives for the methanation of CO2, the technological challenges of the supply of renewable hydrogen and the efficiency in the thermal control of the process, still exist [[7](#_ENREF_7)]. As for the thermal control of the reaction, an alternative is to explore devices such as the structured catalysts, which allow better thermal management of processes, among several other advantages that have been widely described in literature [[8](#_ENREF_8), [9](#_ENREF_9)].

Structured catalysts can improve the performance of fixed-bed systems in terms of mass and heat transfer, and there are different strategies for carrying this out [[10-13](#_ENREF_10)], where several parameters such as materials and design of the structured, structuring methodology and the presence of additives, among others, have to be considered. However, the most important fact to take into account is that during the structuring of a catalyst, changes in their catalytic performance may occur, so it is necessary to evaluate them in order to establish whether such structuring is worthwhile.

Regarding the methanation catalysts, several systems have been studied up to now [[14](#_ENREF_14)] , and the idea of combining the catalytic properties of different metals has inspired the formulation of bimetallic catalysts, which is the case of Ru-Ni catalysts [[15](#_ENREF_15)]. On the one hand, Ru is a highly active metal for Sabatier reaction but its high price limits its use. On the other hand, nickel (Ni) has also exhibited a high level of performance and is considerably cheaper than Ru. Nevertheless, Ni is more sensitive to deactivation by sintering and the formation of carbon deposits [[16](#_ENREF_16)]. Therefore, combining these two metals, a synergy may be produced which would result in in a more resistant catalyst that is better able to reduce the deactivation caused by the formation of carbon deposits.

Considering the above, the present work aims to evaluate the viability of the structuring of a catalyst with a chemical composition suitable for CO2 methanation, using metal micromonoliths. Firstly, the possible effects of the structuring process over the performance of the catalyst will be evaluated. Then, a deeper catalytic evaluation of said structured systems will be carried out, modifying process variables such as catalytic layer thickness, space velocity, process pressurization and the presence of water in the feed-stream.

1. **Experimental Section**
   1. **Catalyst preparation**

It is necessary to clarify that the selection of the catalyst is based on different aspects. Firstly, the fact that Ru and Ni components are the two most common active phases in the methanation catalysts reported in the literature [[17](#_ENREF_17)]. Secondly, the high thermal stability of the support induced by the promoting effect of MgO over the alumina. In addition, the formulation of the catalyst used in this work has been previously evaluated in the dry-steam reforming reaction [[15](#_ENREF_15)]. Therefore, although the analysis conditions of dry-steam reforming and CO2 methanation are quite different, there are features of said formulation that may be useful for both processes. For instance, the fact that Ru inhibits the sintering of Ni, while promoting the gasification of possible carbon deposits, which is something that could occur in methanation reaction. In the same way, the presence of Ru can reduce the operating temperature at which the catalyst works. Accordingly, this work does not pretend to optimize the properties of the present catalyst to improve its performance in the methanation reaction. It is only intended to evaluate the viability of its structuring, on the basis that it is expected to be an active formulation in said reaction.

The powder catalyst was synthesized by means of wet impregnation, following the procedure described by Alvarez et al [[13](#_ENREF_13)]. Firstly, a commercial ɣ-Al2O3 (Sasol, Puralox Scca 1.8/210) was dispersed in an ethanolic solution of magnesium nitrate hexahydrate (Mg(NO3)2·6H2O) (Sigma-Aldrich), in order to obtain a 10 wt% of Mg loading. After 10 min of magnetic stirring at room temperature, the solvent was removed using a rotavapor and the obtained solid was dried at 60ºC for 12h, and finally calcined at 850ºC (10ºC min-1) for 12h. This material is labelled as SUP.

Afterwards, the modified alumina was simultaneously impregnated with an ethanolic solution of two active phases: ruthenium (ruthenium nitrosil nitrate (Johnson Matthey)) and nickel (nickel (II) nitrate hexahydrate (Sigma-Aldrich)) aiming to generate a 15 Ni wt.% and 0.5 Ru wt.%. After 15 min of stirring at room temperature, the solvent was removed with a rotavapor, and the obtained solid was dried at 70ºC overnight and finally calcined at 500ºC for 3 h, with a heating ramp of 10ºC min-1. The catalyst is labelled as CAT.

* 1. **Micromonoliths manufacturing**

For the manufacturing of the micromonliths commercial FeCrAlloy® stainless steel sheets 50 µm thick (Goodfellow® Cr 22 wt.%, Al 4.8 wt.%, Si 0.3 wt.%, Y 0.3 wt.%, C 0.03 wt.%, Fe balance) were used. Firstly, the foils were washed with water and soap, and then with acetone under sonication (30 min). Finally, these were dried at room temperature overnight. The micromonoliths were prepared by rolling two sheets, one flat and the other corrugate, leading to a cylindrical-shaped body (L = 3 cm, Ø = 1.6 cm, 540 cm2 total surface area) with parallel longitudinal channels (2063 cells per square inch). Prior to the deposition of the catalyst, the micromonoliths were treated into an oven at 900ºC for 22 h, in order to generate an homogenous layer of oxide in the metal surface, mainly composed by α-Al2O3 with a typical shape of whiskers that improves adhesion of the catalyst to the walls of the micromonolith’s channels [[18](#_ENREF_18)].

* 1. **Structuring of the catalyst**

The coating of the micromonoliths was carried out through the washcoating method [[19](#_ENREF_19)]. For this, a slurry of the solid CAT was prepared with an optimized formulation that is presented in Table 1. For controlling the particle size, a portion of CAT was milled in a zirconia jar on a Retsch PM100 equipment until obtaining a particle size around 10 µm. The milling conditions were 300 rpm for 30 min with 25 ZrO2 balls (Ø=10 mm). Then, the required amount of milled powder (according to Table 1) was dispersed in deionized water in an ultrasound bath (Sonicator Misomix) for 10 min. Afterwards, polyvinyl alcohol (PVA) and the colloidal alumina (Nyacol Al20) were added as additives aiming to enhance the stability of the suspension. The pH was adjusted to 7.1 with diluted NH3 and the final mixture, with a viscosity of 8.9 cP, was kept under stirring for 24h at room temperature.

**Table 1.** Optimized composition of the slurry

|  |  |
| --- | --- |
| **Component** | **Wt. %** |
| CAT | 18.18 |
| PVA | 1.14 |
| Nyacol AL20  (Al2O3 20 wt.%) | 6.06 |
| H2O | 74.62 |

For the coating of the walls of the channels, the thermally treated micromonoliths were immersed into the slurry for 1 min, with an immersion and extraction constant speed of 3 cm min-1. Subsequently, the excess of colloid was removed by applying a flow of synthetic air (7 bar) during 5 s, to avoid the obstruction of the channels. Then, the coated monolith was dried at 120ºC for 60 min. This process was repeated until the expected catalyst load was achieved. In all cases, a reproducible amount of catalyst was loaded, 66.32 ± 6.03 mg/per coating (Fig. S1). Once the loading of catalysts was achieved (~200 or 400), all the coated micromonoliths were calcined at 500ºC for 3h, with a heating ramp of 2 ºC/min. The different coated micromonoliths were labelled as Mx, where x corresponds to the intended loading in mg of catalyst (X = 200 and 400) after the calcination at 500 ºC. The theoretical and experimental catalyst loading values for each case are presented in the Table 2, as well as the catalytic thickness estimated for both micromonoliths following the methodology reported by Almeida et al. [[20](#_ENREF_20)] .

For comparative purposes, a portion of the slurry was dried and subsequently calcined at 500 ºC for 3h to simulate the thermal treatment of the coating and to be able to characterize this by means of techniques that allow the analysis of the powders. This dry and calcined slurried catalyst is labelled as SLU.

* 1. **Characterization techniques**

Textural properties of the powder catalyst were analyzed in a Micromeritics ASAP 2020 using nitrogen adsorption-desorption isotherms. Prior to measurement, the samples were degassed for 2 h at 250ºC in vacuum. In the case of the micromonoliths, a homemade cell was used that allows an analysis of the entire block. In both cases, the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method [[21](#_ENREF_21)].

The XRD analysis was carried out in an X´Pert Pro PANalytical diffractometer at room temperature. Diffraction patterns were performed using Cu Kα radiation (40 mA, 45 kV), in a 2Ɵ range of 10 to 90º, and a position sensitive detector using a step size of 0.05º and a step time of 300s.

SEM micrographs were obtained in a Hitachi S4800 SEM-FEG high-resolution microscope (1-3 nm) coupled to EDX Bruker X Flash Detector 4010 (133 eV resolution). For cross-section analysis of the micromonoliths, these were cut, embedded in a polymeric resin matrix and polished for carrying out the measurement.

Transmission electron microscopy (TEM) micrographs were obtained with a FEI Talos electron microscope operated at an acceleration voltage of 200 kV, equipped with a Field Emission filament. Micrographs were taken with a side mounted Ceta 16M camera. For the establishment of the particle size distribution of active phases, close to 200 particles from different micrographs were analyzed.

Raman spectra were obtained in a dispersive Horiba Jobin Yvon LabRam HR800 Confocal Raman Microscope with a green laser (λ = 532.14 nm), working at 5 mV power and using a 600 grooves/mm grating. The microscope used a 50x objective with a confocal pinhole of 1000 µm.

The temperature-programmed reduction (H2-TPR) was carried out in a TPR equipment (PID Eng&Tech®). For this, the catalyst (50 mg) was loaded into a U-shape quartz reactor and it was cleaned with an Ar flow (50 mL/min) for 20 min at room temperature. Then, a total flow of 50 mL/min of H2 5 vol.% in Ar was applied over the catalyst while the temperature was raised from room temperature to 900ºC (10ºC/min). A cold trap was set prior to the thermal conductivity detector (TCD) during the entire time in order to condense the produced H2O during the reduction processes. TCD signals and temperature were recorded in each analysis with the program Process@ developed by PID Eng&Tech®.

To evaluate the adherence of the catalytic layer, the coated micromonolith was introduced with ether into a closed flask and subsequently submitted to ultrasound in a Cole Parmer ultrasonic bath (47 kHz and 130 W) for 60 min at room temperature. After that treatment, the micromonolith was dried and the adherence percentage (Ad %) was established, comparing the weights prior and after the sonication treatment. [[15](#_ENREF_15)]

* 1. **Catalytic activity measurements**

The catalytic activity measurements were carried out in a Microactivity Reference PID Eng&Tech® equipment using a 16 mm internal diameter AISI316 stainless steel tubular reactor (Autoclave Engineers®). A constant bed volume of 6 cm3 was set for the powder catalysts, which was comparable to the total volume of the micromonoliths. To reach it, the powder catalysts (CAT or SLU, sieved to a particle size 100 < φ < 200 µm) were diluted with SiC VWR Prolabo® (125 µm). Prior to the catalytic tests, the samples (powders and micromonolith) were reduced with a 100 mL/min total flow of a mixture of H2 50 Vol.% and N2 50 Vol.%, at 400 ºC for 1h. Then, the system was cooled down at 150 ºC with a 100 mL/min total flow of N2. Subsequently, N2 was replaced by the mixture of reaction (with a composition presented in Table 2) and the catalytic conversion was evaluated every 50 ºC up to 400 ºC. Taking into account that several catalytic tests were carried out in which different parameters were varied, Table 2 summarizes the conditions of each of these tests.

**Table 2.** Experimental details of the studied systems and the different catalytic activity tests\*

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Issue of study | Test | Catalytic System | Catalyst Load  (mg) | Average catalytic layer thickness (µm)\*\* | Feed-Stream  Total Flow (mL min-1) | H2O Vol.% in the feed-stream | Pressure  (bar) |
| Effect of the structuring process | T1 | CAT | 200 | 25\*\*\* | 200 | 0 | 1 |
| T2 | SLU |
| T3 | M200 | 2 |
| Effect of the space velocity | T3 | M200 | 200 | 2 | 200 | 0 | 1 |
| T4 | 100 |
| T5 | M400 | 400 | 4 | 200 |
| T6 | 400 |
| Effect of the presence of H2O in the feed-stream\* | T4 | M200 | 200 | 2 | 100 | 0 | 1 |
| T7 | 5 |
| T8 | 10 |
| T9 | 15 |
| Effect of the pressurization | T4 | M200 | 200 | 2 | 100 | 0 | 1 |
| T10 | 2 |

*\*Feed stream composition: CO2 15 Vol.%; H2 60 Vol.% and N2 25, except for T7 – T8, where the corresponding N2 Vol.% was replaced by H2O.*

*\*\*Average catalyst layer thickness (δ) calculated assuming spherical particles according to δ = W·S-1D-1, where W is the mass of loaded catalyst, S the support geometric surface area, and D the washcoat density (1.967 g·cm-3).*

*\*\*\* Apparent catalytic layer thickness: calculated as dp/6 assuming spherical particles (dp is the mean particle diameter for the powder catalysts = 150 µm).*

Regarding reactants and products, these were analyzed via on-line gas chromatography (GC) using a Varian micro GC 4900 instrument with two channels, one of them with a Porapaq-Q and the other with a Molecular Sieve 5 A column. Both channels have a thermal conductivity detector (TCD). The CO2 in the outlet of the reactor was also recorded with a Vaisala® detector CARBOCAP GMT220. CO2 conversion (XCO2) and yields to CH4 and CO were established by means of Eq. 4-6 respectively.

(Eq. 4)

(Eq. 5)

(Eq. 6)

1. **Results and Discussions**
   1. **Characterization of the powder materials and the structured systems**

First, the effect of introducing the catalyst into the suspension to perform the washcoating was analyzed through the comparison of the CAT and SLU systems. The XRD patterns of both powders are presented in Figure 1. Both profiles are quite similar and show the main reflections of the spinel MgAl2O4 (JCPDS 00-021-1152) at 31.2º, 45.8º, 59.3º y 66.2º (JCPDS 00-021-1152) that correspond to the (220) (400) (511) and (440) crystallographic planes. Additionally, in both cases, no reflections associated with MgO can be observed, which suggests no segregation of such oxide.



**Figure 1.** XRD patterns of CAT and SLU, prior and after a reduction treatment

Regarding the presence of Ru and Ni containing species, a reflection generated by RuO2 is observable at 2Ө = 28.17º, 35.30º and 54.32º (JCPDS 00-040-1290). Moreover, three reflections at 2Ө = 37.25, 43.42º and 63.13º can be associated to NiO (JCPDS 00-047-1049). The most remarkable difference between CAT and SLU is that for the latter, there is evidence of sintering of the metallic phases [[18](#_ENREF_18)]. The high intensity of the reflections of RuO2 species and the high intensity of the peak at 37.25º suggests the enlargement of the crystalline domain of such oxide produced by the additional calcination process applied in SLU.

As a complementary study, aiming to observe the effects of the reductant treatment prior to the catalytic activity measurements (400ºC, 1h in H2), the XRD patterns of the reduced CAT and SLU were recorded and included in Figure 1 as Red-CAT and Red-SLU respectively. Firstly, in the case of Red-CAT, the diffraction lines of RuO2 disappear due to the transformation of this phase into metallic Ru, although the reflections of such a metal are not easily observed, probably due to their small proportions. However, for the Red-SLU, some effects of the thermal treatments carried out during the structuring process are observable. For instance, the enlarged reflections produced by RuO2 in SLU do not disappear completely after the reduction. This means that not only larger Ru particles are to be expected in the catalyst that is coating the micromonoliths, but also some unreduced RuO2 species could be present.

Regarding the nickel containing species, the overlapping of the signals with those of the MgAl2O4 makes it difficult to clearly differentiate the evolution of NiOx and Ni species. However, the general trends observed in the region from 40 to 50 º2θ suggest that in the case of the Red-SLU, not all the NiO species were totally reduced, so a mixture of larger NiO and Ni particles can be expected in the catalyst that is coating the micromonoliths.

Finally, after the different XRD experiments were carried out over the CAT and SLU solids, it has to be remarked that no evidence of the alloy formation between Ru and Ni were observed, even in reduced systems. However, it is difficult to establish, in light of our results, whether the Ru is covered by or is under the Ni species, or is directly on the support. To establish this more clearly, additional experiments should be carried out, and we are performing spectroscopic studies using probe molecules in order to clarify the arrangement of the active phases of the catalyst on the surface. Nevertheless, this is a work in progress and as such will be featured in a future paper.

The reducibility of the synthesized samples was studied by H2-TPR, and the results are shown in Figure 2. The profiles obtained for both samples are very similar and three main zones of reduction events can be identified (low temperature zone: 100-250 ºC; medium temperature zone 300-600 ºC; and high temperature zone: 750-900ºC). Despite this, the main difference is that the maximum of the principal reduction events is shifted towards higher temperatures in the case of the SLU solid, which suggests lower reducibility.



**Figure 2.** H2-TPR of the synthetized samples.

In a previous work reported by Álvarez et al. [[15](#_ENREF_15)] the same support as that used in the present study (SUP) was coated with just Ni, and for this material the absence of low temperature reduction events due to the Al2O3, Ni or Mg containing species was demonstrated. Threfore, for both CAT and SLU, the reduction event in the low temperature zone can be attributed to the transformation of Ru4+ into Ru0, and this is in agreement with what has been previously reported in literature. For instance, Balint et al. [[22](#_ENREF_22)] established that the reduction of RuO2 not only occurs at low temperatures but also through different steps. Firstly, the reduction of well-dispersed RuO2 particles (150-180ºC) is achieved, followed by the reduction for RuO2 agglomerates at higher temperatures (200-250ºC). Therefore, the evolution of a signal with a maximum of 212 ºC in the case of the solid SLU, suggests that the structuring process may decrease the dispersion of the species containing Ru, as was observed in the XRD analysis.

The medium and high temperature reduction zones could be due to the reduction of Ni containing species as reported in different works where symilar systems Ni/Mg-Al2O3 have been studied [[15](#_ENREF_15)]. Firstly, in the medium temperature zone, the most intense and broad reduction peak could be attributed to the transformation of NiO into Ni0. Nevertheless, the maximum temperatures for these peaks (438 ºC and 466 ºC for the CAT and the SLU respectively) are clearly below those reported for bare NiO (often around 630 ºC). Hence, this decrease in the reduction temperature of NiO species in the CAT and SLU solids may be attributed to the Ru-Ni interaction in the surface, as proposed by Álvarez et al. [[15](#_ENREF_15)] in their previous study of these types of catalysts. In this case, the authors suggested that, on the one hand, the proximity of Ru and Ni-containing species may promote an electronic effect that reduces the energy required to reduce Ni. On the other hand, they do not rule out that Ru promotes a spillover effect of H2 [[17](#_ENREF_17)] that begins to pass through the sample at low temperatures, due to the intimate contact between the active phases, which manifests itself in the decrease in the Ni reduction temperature.

Then, in the high temperature zone, the reduction of NiAl2O4 spinel is expected [[23](#_ENREF_23)] since the MgO included in the support (10%) creates tetrahedral sites available for the Ni-Al interaction, resulting in Ni atoms that are hardly reducible [[15](#_ENREF_15)]. The temperature where such a reduction event occurs seems not to be affected by the inclusion of Ru in the formultion of the materials, if these are compared with the Ni/MgO-Al2O3 reported by Álvarez et al. [[15](#_ENREF_15)]. Nevertheless, what is clear on comparing the reducibility of CAT and SLU in Figure 2, is that all reduction events of SLU occur at higher temperatures than those of CAT. This result directly correlates with the decrease of dispersion of both types of active phases (Ru and Ni containing species), which was also observed in the XRD experiments.

As for the Raman spectroscopy, the spectra of the SUP, CAT and SLU materials are presented in Figure 2. SUP shows the characteristic bands for MgAl2O4, at 310 cm-1 (T2g), 415 cm-1 (Eg), 672 cm-1 (T2g), 700 cm-1 (T2g) and 772 cm-1 (A1g), which correspond with the five active Raman modes(A1g + Eg + 3T2g) [[24](#_ENREF_24)]. In the case of CAT and SLU, besides the bands of the support, it is necessary to consider the bands corresponding to RuO2 and NiO. For RuO2, the Raman bands appear at 525 cm-1 (Eg), 605 cm-1 (A1g) and 714 cm-1 (B2g) [[24](#_ENREF_24)], while for NiO a wide band towards 500 cm-1 is suggested, which can be assigned to an overlapping of two bands (480 and 555 cm-1) [[25](#_ENREF_25)]**.** Nevertheless, it has to be remarked that NiO Raman bands are difficult to identify due to the overlapping with the bands of the other components of the studied materials in CAT and SLU.

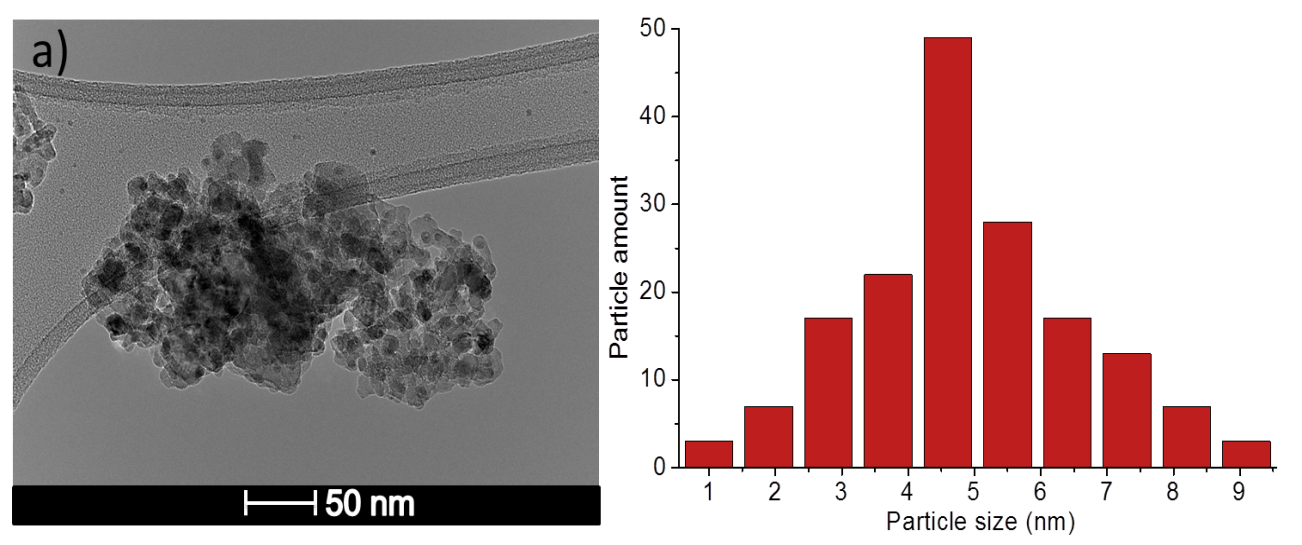


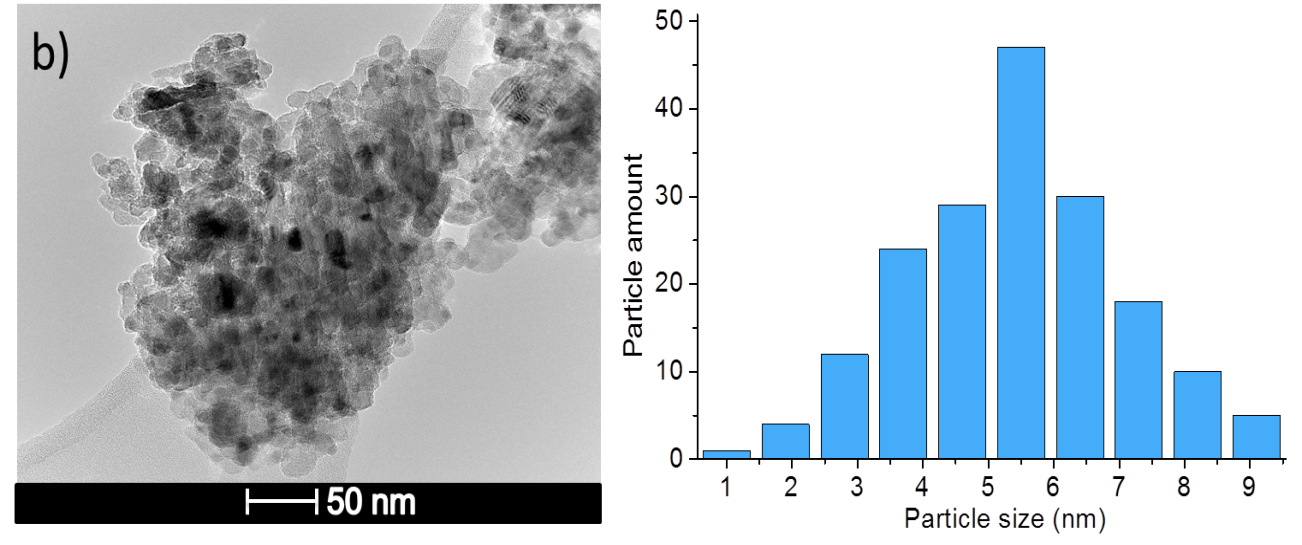
**Figure 3.** Raman shift for powder and slurry catalyst.

In the case of the SLU, a broad low intensity band appeared around 254 cm-1 and this should be due to the contribution of the additional Al2O3 introduced in the formulation of the systems during the structuring process by the addition of Nyacol, because of this additive includes Al2O3. In fact, some authors have described the presence of different low intensity Raman bands which are often overlapped in a broad region (from 250 to 400 cm-1) and produced by vibrations of Al-O bonds in tetrahedral coordination [[26](#_ENREF_26)].

Moreover, RuO2 bands are more intense in the case of SLU than in the powder. The alteration of the vibrational modes of RuO2 due to the modification of the crystallite size of such oxide has been demonstrated by different authors such as Navarro et al. [[27](#_ENREF_27)], who observed modification in the relative intensities of the Raman bands of RuO2 depending on the particle of such oxide. Therefore, the Raman spectra presented in Figure 3 confirms that the structuring process induces sintering of the active phases of the catalysts, as was observed in the XRD and TPR experiments.

It has to be remarked that although in the reduced materials both active phases (Ru and Ni) must be present, the analysis by TEM has been focused on the Ni species. Therefore, different micrographs such as those included in Figure 4, were obtained for Red-CAT and Red-SLU that allowed the particle size distribution of Ni particles to be established. In all cases, the chemical composition of the selected particles was confirmed through EDX analysis such as that presented in Figure 5, where the homogeneous distribution of Al, O and Mg can be confirmed, as well as the presence of clusters of Ni. Regarding Ru, although this element is present in the studied materials and was considered in the EDX analyzes, it was not possible to find areas where this element would be present. This is due to the low concentration of Ru in the material, which makes it difficult to identify.





**Figure 4.** TEM micrographs and particle size distributions for: **(a)** Red-CAT and **(b)** Red-SLU

The calculated average Ni particle size for Red-CAT and Red-SLU (4.6 nm and 5.5 nm respectively) and the shift of particle population towards larger sizes in the distributions of the Red-SLU, demonstrates that the sintering induced during the structuring process also affects Ni species.



**Figure 5.** Representative EDX analysis carried out over the Red-CAT

The textural properties (the specific surface area (SBET), the pore volume (Vpore) and the average pore diameter (PD) of the powder materials (SUP, CAT and SLU), summarized in Table 3, were extracted from the N2 isotherms included in Figure 6. The micromonolith, M200, was studied thanks to the experimental setup.

**Table 3.** Textural properties for the powder and the structured catalyst.

|  |  |  |  |
| --- | --- | --- | --- |
| **Material** | **SBET (m2/g)** | **Vpore (cm3/g)** | **PD (Å)** |
| SUP | 123 | 0.37 | 89 |
| CAT | 114 | 0.30 | 87 |
| SLU | 103 | 0.28 | 77 |
| M200φ  Al2O3 NyacolΩ | 107  192 | 0.28  0.37 | 82  78 |
| φ The amount of adsorbed N2 was normalized by the loading of coated catalyst, discarding the contribution of the metallic block.  Ω Nyacol AL20 dried and calcined at 400ºC 2h | | | |



**Figure 6.** **(a)** N2 adsorption-desorption isotherms and **(b)** Pore size distribution of the SUP, CAT, SLU and M200.

Firstly, the isotherms of all the studied systems can be classified as type IV [[28](#_ENREF_28)], which suggests that the mesoporous character of the materials in all cases, both prior to and after the structuring process, has been maintained. Regarding the hysteresis, this can mainly be classified as H1 type in all cases that suggest a configuration of aggregates or agglomerates of spheroidal particles. However, it is evident that such behavior is altered in the case of the SLU and the M200 systems, due to the presence of the additional alumina Nyacol, and probably a mixture of H1 and H3 hysteresis is occurring due to the modification of the pore size distribution, which becomes more heterogeneous.

Regarding the pore size distribution Figure 6b, a unimodal distribution centered around 10 nm is observed for the SUP, which is maintained for the other systems. However, the calcination processes after Ru and Ni deposition for the CAT system, and the additional process at 500 ºC for the solid SLU, can generate an initial decrease in pore volume, as well as a slight widening of the trends. In the case of the SLU and M200 systems, the additional decrease of the pore volume could be produced by the inclusion of Nyacol, as was suggested above, although the alterations do not seem very severe. Therefore, the preservation of pore size distribution in the structured systems confirms that the structuring process does not significantly affect the porous structure of the original catalyst.

Further characterization of one of the obtained monoliths was carried out including the XRD analysis of a portion of the coated walls (See Figure S2). For this study it was necessary to disassemble the monolith. The results are presented in the supplementary information, and this also includes a broader discussion of what was observed. As a remarkable feature, it was observed that the XRD analysis confirmed the evolution of the Al2O3 phase over the surface of the thermally treated monolith. Additionally, the presence of the crystallographic phases of the SLU are present in the case of the structured system, as well as those of the main components of the metallic substrate. Moreover, by means of SEM the homogeneous covering of the metallic substrate with a layer of Al2O3  was confirmed, with the needles morphology allowing the anchoring of the catalyst particles in the walls of the channels (See Figure S3).

Another relevant aspect that has to be analyzed in coated structured catalysts is the thickness of the coating. For the studied micromonoliths, the estimation of the thickness of the catalytic layer is particularly difficult, this is due to the contribution of the alumina generated over the metallic substrate by the thermal treatment prior to the coating process. However, the in-line analysis using a SEM micrograph oriented to one of the edges of a sheet coated with SLU, such as that presented in Figure 7 for the micromonolith M200, allows an acceptable estimation to be obtained of the thickness of the Al2O3 layer generated over the surface of the micromonolith prior to the washcoating, in addition to that of the catalytic layer. As for the oxidation layer, a thickness of 3 μm was established in the zone where the concentration of Al increases, while for the catalytic layer, a thickness of 3.5 μm could be assumed in the region where the maximum Al concentration is maintained. Following a similar procedure for the micromonolith M400, a catalytic layer thickness of around 5.4 μm was estimated. Therefore, comparing the thicknesses obtained for both structured systems by means of TEM and those calculated using the density of the slurried catalyst and the geometric area of the monoliths (Table 2), there is an overestimation of around 1.5 μm when using the TEM analysis. However, taking into account the possible errors of both estimation methodologies, these values are very close to each other, which allows us to affirm that they are very close in reality.



**Figure 7.** In-line analysis of one of the edges of a sheet coated with SLU, obtained from a dissembled micromonolith, M200.

* 1. **Catalytic activity measurements**

As stated in the experimental section above (Table 2), different catalytic tests were planned with the aim of analyzing different issues, and the first one is to carry out a general comparison between the powder materials and the structured ones. Therefore, in Figure 8, the CO2 conversion of the powder materials and that of M200 is presented (Tests T1-T3 / See Table 2), while Figure 9 presents the yields to CH4 and CO. In these experiments, the same amount of catalyst and total flow of the mixture of reaction were constant (200 mg and 200 mL/min).



**Figure 8.** CO2 conversion of the studied systems in Test 1-3

The three studied materials present similar trends that exhibit an increase of the CO2 conversion with the temperature, without reaching the equilibrium conversion in the analyzed temperature range. However, a more detailed analysis shows that the solid SLU exhibits a slight loss of activity from 300 ºC and the micromonolith is even slightly lower in the conversion levels from 250ºC.



**Figure 9.** Yields to CH4 and to CO of the studied systems in Test 1-3

Prior to the analysis of the yields of CH4 and CO, it should be mentioned that the selectivity of both products was also estimated. However, no relevant differences between CAT, SLU and M200 were observed. This is why the yield criteria were preferred as, although it does not show great changes either, it allows us to better see the small differences between the systems.

In all cases, the yields of CH4 and especially CO (Figure 9) are quite similar, although slightly higher toward the production of CH4 in the case of CAT. Nevertheless, this difference can almost be ruled out. Therefore, the structuring process appears to influence the conversion levels slightly more without altering the yield of CH4 and CO. Furthermore, taking into account that the characterization of the starting catalyst (CAT) and the slurried one (SLU) allowed it to be established that the sintering of the active phases was the main modification during structuring, this may also be the reason for the slight drop in catalytic activity.

As mentioned above, further experiments are needed to clearly establish the arrangement of the active phases on the surface of the catalyst. However, sintering of both Ni-containing and Ru-containing species during structuring was confirmed by XRD, TPR and Raman. Although taking into account what has been previously reported, we could be in a situation where the effects of sintering on the active phases may be offsetting, since it is widely accepted that sintering can decrease the catalytic performance of Ni catalysts [[14](#_ENREF_14)]. On the other hand, it could be beneficial in the case of Ru, which has been demonstrated in different cases such as that reported by Navarro-Jaén et al. [[27](#_ENREF_27)], where they observed that the larger Ru species the higher the CO2 conversion.

In addition to the possible dual effect of sintering, based on the characterization of the materials, the question arises as to how comparable the powder catalysts and the monoliths are. Regarding this, it is important to say that although most of the experimental variables remain fixed in all cases, the particle size of the powder catalysts is not the same as that of the structured ones. If an apparent layer thickness is estimated from the average particle size of the powder catalysts (150 μm), a value of around 25 μm is obtained. This means that CAT and SLU systems operate almost as a structured system with a 25 μm catalytic layer, while the M200 monolith has a thickness of 2 μm. Such a low thickness in the M200 may have promoted changes in catalytic activity in either a positive or negative way, nevertheless, more experimentation is needed to clarify this question.

Regarding the experiments focused on the influence of the space velocity (Test T3-T6, see table 2), these allowed a comparison of the weight hourly space velocity (WHSV) included in table 4, and the results of CO2 conversion and yields of CH4 and CO are presented in Figures 10 and 11 respectively.

**Table 4.** Parameters analyzed by modifying the catalyst face and the total reaction flow

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Test | Monolith | Total Flow  (mL/min) | Total Flowα  (g/min) | WHSVβ  (1/h) |
| T3 | M200 | 200 | 0.1323 | 40 |
| T4 | M200 | 100 | 0.0661 | 20 |
| T5 | M400 | 200 | 0.1323 | 20 |
| T6 | M400 | 400 | 0.2645 | 40 |

αWeight flow rate expressed in mass of the reaction mixture per unit of time

βWHSV = Weight flow rate to weight of loaded catalyst ratio



**Figure 10.** Effect of the space velocity in the CO2 conversion of the studied systems in Tests T3-T6.



**Figure 11.** Effect of the space velocity on the yields to **(a)** CH4 and **(b)** to CO

The results demonstrate that only in the case of the WHSV = 20 h-1, the two tested monoliths present a similar conversion, while for WHSV = 40 h-1, not only is a lower conversion seen in both cases, but there is also a discrepancy in these trends. These results suggest that there are no critical effects of transfer limitations in the experiments with WHSV = 20 h-1, from the point of view of criteria such as that of Madon-Boudart [[29](#_ENREF_29)]. However, in the other two cases with a higher WHSV, there are transfer problems. Therefore, taking into account the fact discussed above that the estimated catalytic layer thickness in the two studied monoliths is quite low, since it is below 5 µm, that the transfer problems are of a mass type can be ruled out . In this sense, the discrepancies in the WHSV = 40 h-1 experiments could be due, in the first instance, to a very low residence time, which does not allow the reactor to carry out the process effectively. Moreover, we could be facing phase transfer limitations due to thermal gradients [[30](#_ENREF_30)].

This last statement, of course, requires a more in-depth study that includes a deep kinetic analysis with the measurement of thermal profiles inside the monolith during the reactions, and this is not part of the scope of this paper. Additionally, the manufacturing material of the monoliths, their thermal conductivity and the design of the structure itself must be considered, analyzing variables such as cell density and total reactor volume. However, the results of yield of CH4 and CO (Fig. 11) may be in line with these claims. In fact, they reveal more clearly the differences between the studied systems such as the fact that the M400 monolith studied with a WHSV = 20 h-1, presents the highest yield of CH4 and the lowest yield of CO. Furthermore, it is observed that the discrepancies between all systems become more pronounced as the temperature increases (> 325 ºC), which occurs when the competition between the CO2 methanation and the R-WGS reaction becomes more significant. Hence, deficiencies in thermal control seem to manifest more sharply at high temperatures. In any case, what is clear is that in this catalyst structure feasibility study, it can be established that working under conditions of WHSV = 20 h-1 for loads between 200 and 400 mg of catalyst, seems to minimize the effects of mass transport limitations for this monolith design coated with this catalyst.

Another component that plays an important role in the Sabatier reaction is water. Firstly, water is one of the products of the methanation reaction as well as of the R-WGS reaction. In addition, it can compete with other reagents as one more adsorbate to anchor to active sites. Moreover, its ability to promote sintering of metal particles at high temperatures is known [[14](#_ENREF_14)]. Despite this, there is evidence that water can avoid the deposit of carbon over the catalyst surface [[31](#_ENREF_31)] by means of the promotion of gasification processes [[32](#_ENREF_32)], so it is interesting to evaluate its influence over the catalytic performance when it is included within the feed-stream during the Sabatier reaction. Therefore, the M200 system has been tested under different feed-streams modifying the amount of water (Tests T4, T7-9 – See Table 2), and the conversion values are presented in Figure 12.



**Figure 12.** Effect of the inclusion of water (Tests: T4, T7-9) in the CO2 conversion of the M200 monolith

Figure 12 shows that while the amount of water increases in the feed-steam, the conversion decreases, in agreement with the thermodynamic calculations. This behavior is confirmed by the decreasing of the yield of CH4 and CO with the inclusion of water in the mixture of reaction (Figure 13).



**Figure 13.** Effect of the inclusion of water (Tests: T4, T7-9) in the yield of: **(a)** CH4 and **(b)** CO.

These results may firstly be explained in terms of a modification in the reaction equilibrium, since water is a product of Sabatier reaction, and as such its incorporation in the feed of the reaction disturbs the equilibrium according to Le Chatelier´s principle. Although the yield of CH4 decreases, the yield of CO decreases in the same order, due to the fact that the R-WGS equilibrium is altered, too [[32](#_ENREF_32)]. However, we must not neglect the possible sintering that water promotes on metallic species and, in turn, the dual effect that this can cause in this catalyst. In this case, the drop in activity depending on the incorporation of water, would indicate that it mainly affects Ni species because they increase in size [[33](#_ENREF_33)]. The other possible effect of water is its oxidizing capacity, which could be oxidizing the active species and thus decreasing its catalytic performance [[34](#_ENREF_34)]. So, from what can be seen, water has different options to reduce the catalytic performance of the structured M200, although in this case, the loss of activity was not so important. What is clear is that additional analyses are needed in order to know which of these mechanisms bears the main responsibility for the loss of activity due to the presence of water.

Pressurizing the Sabatier reaction may also affect the catalytic performance of the studied systems, since the yields of CH4 proceeds via gas contraction, so the increase in pressure can be expected to increase the equilibrium conversion. Thermodynamically, pressurization produces an increment in the CO2 conversion and the selectivity towards CH4. Yield of CO is expected to decrease, since in the R-WGS reaction the contraction in volume does not occur. Therefore, a pressurized experiment was compared with another, which was carried out at atmospheric pressure (Tests T4 and T10 – See Table 2) and the results are presented in Figures 14 and 15.



**Figure 14.** Pressure effect in the CO2 conversion for the M200 system in Tests T4 and T10.



**Figure 15.** Pressure effect on the yield of: **(a)** CH4 and **(b)** CO.

Pressurization (2 bar) resulted in the increase in the CO2 conversion when compared with that of the test carried out at atmospheric pressure. In addition, a superior yield of CH4 was observed but, most importantly, a remarkably lower yield of CO. This confirms that pressure favors the hydrogenation processes and inhibits the collateral reaction of CO production [[14](#_ENREF_14), [27](#_ENREF_27), [35](#_ENREF_35)]

Finally, a stability test was carried out over the M200 system. The reaction was carried out for 100 h on stream at 350ºC (temperature where the M200 achieved a CO2 conversion near to 50% - see Figure 10) with 100 mL/min of a feed-stream with the same composition of test T4 (see Table 2) and the results are presented in Figure 16.



**Figure 16.** Stability test for M200 at 350ºC. Feed-stream composition (Test T4 – see table 2)

The experiment reveals a behavior that shows slight oscillations, but in general there is a stability in the behavior of the activity, which can be confirmed around 45% and a selectivity near to 95% towards CH4 production, both maintained during the 100 h of the analysis. Therefore, the structured catalyst in the M200 micromonolith shows a promising performance in terms of stability. Considering that in these types of long-term reactions the high exothermicity of the reaction could cause hot spots along the catalytic bed and provoke carbon deposition over the catalyst surface, in this sense, for the tested micromonolith such carbon deposition can be discarded. Nevertheless, further characterization of the monoliths after reaction is required in order to completely rule out this theory and see what state the catalyst is in after more long-term use.

Finally, considering the suitable performance of the structured catalyst that was evaluated under different reaction conditions, it is interesting to compare the results with other ruthenium and nickel catalysts for the Sabatier reaction that previous research has reported. This comparison is not so easy because the differences in the experimental conditions of the catalytic tests applied to each system can influence the result. Furthermore, the composition of the catalysts and their physicochemical properties can alter their performance. Therefore, the activation energy (Ea) is selected as a standardized comparison criterion that allows us to establish where the catalyst of the present work is positioned. The apparent energy activation (Ea) of the M200 system was established through the Arrhenius plot presented in Figure 17. TOF values were calculated from the converted molecules of CO2 (CO2 conversion < 20%) per atoms of active phase, considering this as the sum between the Ni atoms and the Ru atoms.



Figure 17. Arrhenius plot for the structured catalyst.

From the Arrhenius plot, an apparent Ea for the M200 was calculated (77.24 kJ mol-1), and taking into account the presence of two active phases, it is necessary to consider the monometallic systems reported. In the case of ruthenium catalysts, Brooks et al. [[36](#_ENREF_36)] reported an Ea of 69.06 kJ mol-1 over Ru/TiO2, while Prairie et al. [[38](#_ENREF_38)] obtained an activation energy of 79 kJ mol-1 for Ru/TiO2 and Ru/ɣ-Al2O3. In the case of nickel systems, Goodman et al [[37](#_ENREF_37)] reported values of around 88.61 kJ mol-1.

The Ea values of the cited catalysts with only one of the active phases are very close to each other and the M200 system is in an intermediate situation. Therefore, it can be established that this system is comparable to those in previous published research. Although it does not generate a significant decrease in the temperature at which the reaction starts, it is important to note that the structuring process does not significantly alter the properties of the catalyst and is completely comparable with other catalytic systems.

1. **Conclusions**

The structuring process of the selected catalyst (0.5% Ru-15%Ni/MgAl2O4) in metal micromonoliths was successfully carried out. However, some properties of the original catalyst were altered during the deposition process. Comparing the initial powder (CAT) with the suspension prepared for the deposition (SLU), there is evidence of sintering of the active phases containing Ni and Ru, which was confirmed by means of XRD, TPR and Raman spectroscopy. However, the textural properties of slurried catalyst seemed to be unaltered by the structuring process. Although the structuring may slightly modify the physicochemical properties of the starting catalyst, the lower catalytic thickness (below 5 μm) coated in the structured systems M200 and M40 may compensate such modification by means of minimizing the mass transfer limitations.

Regarding the different parameters studied in the catalytic tests, it was observed that only in the case of WHSV = 20/h, mass transport limitations can be minimized, while for the higher value of WHSV evaluated (40/h), transport problems were evidenced, most probably heat transport. Although this is still to be confirmed through further experiments.

As for the presence of water in the feed-stream, a certain decrease in the CO2 conversion and the yield of CH4 were observed for the micromonolith M200, and this was associated to the promotion of sintering and/or to the oxidation of the active phases promoted by water. Furthermore, as expected, pressure has a positive effect upon the catalytic performance of the structured catalyst, increasing not only the CO2 conversion but also decreasing the yield of the undesired product CO. Moreover, the long-term analysis of the catalytic activity of the structured system revealed its high stability during 100h of continuous operation. Therefore, it can be stated that the selected catalyst can be structured by the procedure reported, and that said process does not generate relevant alterations in the performance of such catalyst in the Sabatier reaction. Furthermore, the structured system has a performance comparable to that of other catalysts for this reaction, which have been previously reported in literature.

1. **Acknowledgements**

Financial support for this work has been obtained from the Spanish Ministerio de Ciencia, Innovación y Universidades co-financed by FEDER funds from the European Union (RTI2018-096294-B-C33). Moreover, O.H. Laguna thanks the financial support provided by the University of Jaén through the “Acción 6 del Plan de Apoyo a la Investigación de la Universidad de Jaén (2017-2019)”.

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