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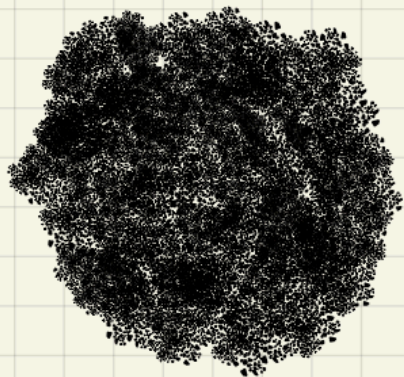
Research Highlights

- The structuring of a Ru/TiO₂ catalyst was carried out using metal micromonoliths.
- The structured catalysts active in the selective CO methanation reaction.
- Different parameters were analyzed during catalytic activity measurements.
- The structured catalyst presented a high catalytic stability in long-term analyses.
- The structured catalyst exhibited high tolerance to shut-down/start-up cycles.
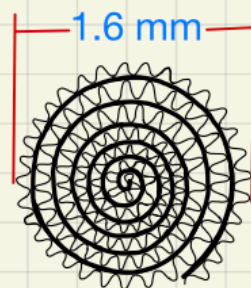
Metal micromonoliths for the cleaning of H₂ by means of methanation reactions

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Abstract

The present manuscript presents for the first time the structuring of a Ru/TiO₂ catalyst that was achieved by means of the washcoating procedure using homemade metal micromonoliths (Fecralloy®) of 1330 cpsi. For this, an optimized formulation of the slurried catalyst as well as a reproducible protocol for the coating of the micromonoliths were successfully achieved. The obtained structured systems were tested in the selective CO methanation reaction and the effect of different variables over the catalytic performance were analyzed such as the amount of loaded catalyst in the micromonoliths, the temperature of reaction, the space velocity, and the amount of CO and H₂ within the feed-stream. The study of all of these parameters allowed to establish optimal conditions to maximize the performance of the structured Ru/TiO₂ catalyst and subsequently, this was tested under those cited conditions in long-term tests (~375 h), including shut-down/start-up cycles, aiming to evaluate its catalytic stability. The system presented a

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considerable stability along the different test without loss of catalytic activity, being specially remarkable its resistance to the inclusion of shut-down/start-up cycles. Therefore, this study lays the foundations for future development of more sophisticated structured systems for the selective CO methanation based on the structuring strategy proposed.

1.   Introduction

The production of H_2 as an energy vector within the principles of renewability and sustainability relies on the development of an efficient technology able to carry out such production with higher energy efficiency and thus requiring the minimum economic investment [1]. In this sense, obtaining hydrogen from organic molecules of renewable origin is an interesting strategy, but it requires purification processes of the stream of H_2 to remove the remnants of CO generated during the reforming of the cited molecules. In addition, the purity levels required for the use of H_2 as fuel cell feed can be high if it is, for example, those of the proton-exchange membrane fuel cell type (PEMFC), which do not tolerate levels of CO> 20 ppm [2].

The preferential oxidation of CO by the inclusion of small amounts of O_2, is a catalytic process often carried out for the final clean-up of H_2 [3]. However, the methanation is an interesting alternative because it does not involve the addition of a different reactant to the reactive current [4]. Only a small part of the H_2 that is in excess in the stream is used to transform the CO into CH_4 (according to Eq.1) which has no negative effect on the PEMFC.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_{298}^o = \text{- 206 kJ/mol} \qquad\qquad \text{(Eq.1)}$$
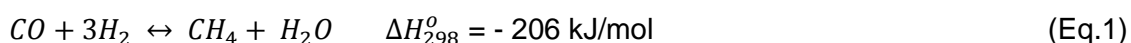
As pointed out by Abdel-Magged et al. [5], due to the high CO_2 contents in the typical reformate gases, methanation catalysts should be not only active but also highly

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selective to methanize CO instead CO_2, aiming to avoid intolerable H_2 consumptions. This is why different catalytic systems have been successfully tested in the CO methanation reaction and within the typical catalyst configuration, Ni [6], Fe [7], Pt [8] and Ru [9] can be the most common active phases, while Al_2O_3 [10], CeO_2 [6] and TiO_2 [9] are the most often used supports.

The Ru/TiO_2 system has been deeply studied in the selective CO methanation process by Verykios and coworkers [11-13]. This system has widely shown to be one of the most active and selective in the cited process thanks, among other aspects, to the strong interaction between the active phase (Ru) and the support (TiO_2) that allows greater stability of the catalytic performance. These authors, along with others [5, 6, 9, 14] who have also analyzed this catalytic system, have managed to establish a clear correlation between the catalytic performance and the physicochemical properties of this type of materials. However, the possible application of this catalyst configuration on a larger scale or in a device that integrates the methanation unit within an integrated circuit for the production of hydrogen by reforming, purifying and using such hydrogen to generate electricity requires a different strategy than generating a powder catalyst.

Therefore, the structuring of powdered catalysts emerges as a promising strategy that constitutes an intermediate step between the laboratory development of a catalyst and the consolidation of the engineering of the process. The benefits of structured catalysts have been widely discussed and analyzed by different authors [15-17]. Among the main advantages are, for example, the reduction of pressure drops that are typical in powder catalysts used in fixed-bed configurations, as well as the intensification of the processes, thanks to the possibility of carrying out a reaction in smaller spaces, with greater efficiency in the heat and material transport processes.

In this context, the role of the substrate material on which the catalyst is structured becomes of significant importance in the process. In the case of CO methanation, which is an exothermic process, a substrate is required that is capable of promoting efficient heat transfer. Therefore, the use of metal substrates, can be a good choice, taking into account their high thermal conductivity.

Despite the enormous potential of the catalyst structuring process, the different stages needed for it can modify the catalytic performances of the starting catalytic formulation, increasing or decreasing them [10]. For this reason, it is pertinent to explore different structuring strategies, taking care of each of the steps that give rise to the structured system.

According to the scenario described above, the present work aims to evaluate the structuring of a catalyst with a Ru/TiO_2 formulation for the selective methanation of CO and to analyze the catalytic performance of the structured system, using steel micromonoliths as substrates. It is important to note that it is based on the knowledge that this formulation is active in the aforementioned reaction, but there are no analyses on the structuring of this system. Therefore, the structuring process carried out is described and a broad catalytic study is performed in which different process variables such as catalyst loading, space velocity, CO and H_2 content in the feed-stream and stability during long-term tests, are analyzed.

2. Experimental Section

2.1. Synthesis of the catalyst

The Ru/TiO_2 catalyst was synthetized by means of the wet impregnation method as reported in [18]. For this, the adequate amount of Ruthenium (III) nitrosyl nitrate solution (Johnson Matthey ®) was diluted with distilled water aiming to achieve a loading of 10 wt.% Ru in the catalyst. The diluted Ru (III) solution was then mixed with Aeroxide® TiO_2

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P25 (5 mL of diluted Ru solution per gram of TiO_2) and a suspension was obtained by means of stirring during 15 min. Subsequently, water was removed on a vacuum rotary evaporator and the obtained solid was dried at 120 ºC for 30 min and finally calcined at 400 ºC for 2 h (heating rate = 10 ºC/min). From this point, the Ru/TiO_2 catalyst will be labelled as CAT along the document.

2.2.   Manufacturing and coating of the metal micromonoliths

Firstly, homemade cylindrical micromonoliths (3 x 1.6 cm) with parallel channels were manufactured, consisting of 50 μm Fecralloy® corrugated sheets (FrCr22Al5, GoodFellow). The procedure for the manufacturing of this kind of structured devices has been previously reported by Sanz et al. [19] and specifically micromonoliths with the following specifications have been used for the present study: cell density (cpsi) = 1330; geometric surface = 420 cm^2; hydraulic diameter μm = 475; porosity (ε%) = 83. Afterwards, the manufactured micromonoliths were cleaned with distilled water and soap, thoroughly rinsed with water and acetone and finally dried at 120 ºC. Then, these devices were thermally treated in air at 900 ºC during 22 h, aiming to create a α-Al_2O_3 layer on the surface of the metal substrate that will result in the improvement of the anchoring of the CAT during the coating procedure [20].

The washcoating procedure was used for coating of the micromonoliths with CAT [20, 21]. For this, a stable slurry of CAT was prepared, and this requires to adjust parameters such as the type of dispersant phase, the particle size, the isoelectric point (IEP), and the concentration of CAT. Firstly, it has to be pointed out that all the experiments were carried out with distilled water, which proved to be a suitable dispersing medium in all cases. Regarding the particle size of CAT, a first analysis of the powder without any milling treatment, showed a single mode distribution (presented in Figure 1A) with average particle size d_{90} = 6.5 μm, which is below 10 μm, the upper recommend limit for

preparing stable slurries [22]. The Zeta potential as a function of the pH was measured to determine suitable pH values to ensure the stability of the slurry. According to Figure 1B, it was established that the IEP for CAT is ca. 5.4. Therefore, the pH = 4 was fixed as the suitable value for ensuring high values of Z potential aiming to promote high repulsion between the CAT's particles, and consequently a higher stability of the slurry.

Figure 1

Moreover, some additives were integrated into the formulation of the slurry, aiming to modulate the slurry viscosity, to promote the adherence of CAT to the metal substrate of the micromonoliths, as well as the washcoating drying process. In this sense, a small amount of colloidal alumina (Nyacol® Al20) was included to enhance the CAT adherence, while polyvinyl alcohol (PVOH) was added to prevent crack formation during the drying of the layer of CAT coated over the micromonoliths. The optimization of the slurry, the composition of which is presented in Table 1, also involved the study of the homogeneity of the coating generated over the walls of the micromonoliths. For this, coated micromonoliths were disassembled and carefully studied (results not presented) and in all cases, optimal coating was achieved without preferential accumulations or uncoated areas.

Table 1.

The thermally treated micromonoliths were dipped into the slurry for 60 s and withdrawn at controlled speed (3 cm/min) [19]. The excess slurry was removed by applying a stream of pressurized air (0.5 bar) at 15 cm from the coated micromonolith for 5 s. The coating procedure was repeated several times, including a drying stage at 120 ºC for 30 min between coatings, until reaching the intended loadings of CAT (~200 and 400 mg) [19]. Finally, the coated micromonoliths were calcined at 400 ºC for 1 h.

2.3. Catalytic activity measurements

Regarding the performance of the structured micromonoliths in the CO methanation reaction, the influence of different parameters such as the loading of CAT, the space

velocity or the concentration of CO and H_2 in the mixture of reaction, were analyzed as well as the stability in long-term tests, including shut-down/start-up cycles. Therefore, the general conditions of both the measurement equipment and the common parameters in all the catalytic tests will be presented, followed by a summary of the specific conditions studied in the particular cases.

In all cases, selective CO methanation measurements were carried out in a Microactivity PID Eng & Tech® Microactivity Reference equipment, using a tubular reactor (Hastelloy - Autoclave Engineers®) with 16 mm internal diameter. Regarding the reaction temperature, a type K thermocouple was used located in the external part of the reactor coinciding exactly in the zone that corresponds to the middle zone of the micromonolith. The recording of the temperature inside the monolith was carried out with another type K thermocouple, which measurement zone was located right in the middle of the axial axis of the monolith throughout the test.

Before reaction, the micromonoliths were activated at 300 ºC for 2 h with a total flow of 60 ml/min of pure H_2. Then, the temperature was decreased while the system was purged with 100 mL/min of N_2. Afterwards, the activation feed-stream was switched to the reaction mixture, which composition simulates a typical output stream of a water-gas shift (WGS) unit (the compositions of the different mixtures of reaction used are presented in Table 2). The Microactivity Reference equipment allows to operate in pressure control mode thanks to an automated pressure release valve in case of over pressure, for which the atmospheric pressure was set as the working pressure in all the catalytic tests. Moreover, reactant and products were analyzed by on-line gas chromatography (GC) using a Varian® Micro GC 4900 instrument equipped with two channels: one with a Porapaq-Q and another with a Molecular Sieve 5A column, each with a thermal conductivity detector (TCD). CO_2 was recorded with a CO_2 IR analyzer, Vaisala® CARBOCAP GMT220. CO and CO_2 conversions (xCO, xCO_2), and selectivity to CO methanation (SCO/CO_2) were defined according to Eq.2-4, being F_{CO},

F_{CO_2} and F_{CH_4} the flows in ml/min of CO, CO₂ and CH₄ respectively, while subscripts *in* or *out* mean the inlet or the outlet flow.

$$xCO(\%) = \frac{(F_{COin} - F_{COout})}{F_{COin}} \times 100 \qquad \text{(Eq.2)}$$

$$xCO_2(\%) = \frac{(F_{CO_2\,in} - F_{CO_2\,out})}{F_{CO_2\,in}} \times 100 \qquad \text{(Eq. 3)}$$

$$Selectivity\ to\ CH_4(\%) = \left(\frac{F_{CH_4\,out}}{xCO \times F_{COin}}\right) \times 100 \qquad \text{(Eq. 4)}$$

As stated above in the introduction section, several experiments were carried out aiming to maximize the performance of the structured micromonoliths by means of modifying different experimental variables. Therefore, detailed information of all the experiments is summarized in Table 2.

Table 2.

In addition to all the experiments carried out to evaluate the effect of all the parameters cited so far, the stability of the catalyst over long periods of use is a determining factor when evaluating its potential as a candidate to be taken to a higher production scale. For this, a feed-stream (CO (300 ppm); H_2 60 Vol.%; CO_2 21 Vol% 21; H_2O Vol.% 16; N_2 for balance) was selected since it simulates the emission of a hydrogen purification unit based on the preferential oxidation of CO (PROX unit), which would feed a methanation unit prior the feed of a PEMFC.

As for the temperature, the value of 180 ºC was selected to avoid reaching a 100% CO conversion and thus be able to obtain results ensuring that all active sites are working at their maximum capacity. Under this same criterion, a space velocity of 1.333 m^3/[kg·s] was selected for this experiment, aiming to ensure that the micromonolith (0.5 mg/cm²)

In this way, a stability experiment was programmed for 340 h, but it is important to note that two shut-down/start-up events were included in which the micromonolith was cooled to room temperature and the flow of reactive mixture was cut off, to clean the columns of the gas chromatograph that was used to monitor the reaction products. In addition, it has to be remarked that when restarting the process, which is, when the catalyst was heated again and the reaction mixture was fed again, no reactivation process was carried out.

3. Results and Discussions

3.1. Modification of different variables during the catalytic activity measurements

3.1.1. Effect of the amount of loaded CAT in the structured systems: In previous studies of structured catalysts for different reactions, it has been demonstrated the strong influence of the thickness of the catalytic layer over the performance of those devices, since such parameter can directly alter the mass and heat transport phenomena during the catalytic reaction [23]. Because of that, it is important to study the influence of the specific CAT loading in the CO methanation for the proposed structured micromonoliths. For carrying out this, two micromonoliths were coated with 216 and 441 mg of CAT, whose represent specific loading ~ 0.5 and 1.0 mg/cm^2 respectively for the two coated structured devices (see Table 2), if the weight of loaded CAT is divided by the geometric area of the structured systems (420 cm^2). The results of CO conversion and H_2 consumption for the two analyzed loadings (Markers M1-M8, see Table 2) are presented in Figure 2.

Figure 2

Both samples present an increment of the CO conversion (Figure 2A) with temperature, which is a behavior also observed in other studies carried out over Ru/TiO_2 powder catalysts tested in the selective CO methanation [11, 12]. Nevertheless, the system with the lowest loading of CAT (0.5 mg/cm^2) exhibits a superior performance at temperatures below 200 ºC. Despite this, neither of studied monoliths achieves a level of CO conversion lower than 20 ppm, the typical requirement of PEMFC, at temperatures below 200 ºC.

Regarding the H_2 consumption (Figure 2B), which must be minimized as much as possible, shows a dramatic increases with temperature in both cases, although the monolith with 0.5 mg CAT /cm^2 produces a slightly lower consumption. Additionally, as a complementary criterion, the H_2 consumption = 4% was highlighted in Figure 2B since this could be set as the upper limit accepted for a methanation unit integrated in a fuel processor unit. This value was obtained by simulations (not provided in the present document) obtained with computational tools (Aspen Plus®), taking into account mass, energy and economic balances. Under this criterion, acceptable values are only reached at temperatures below 190 ºC in the two cases analyzed [24].

Moreover, given the presence of both CO and CO_2 in the reactive stream, it is important to establish whether the consumption of hydrogen is selectively oriented towards the hydrogenation of CO, or whether methanation of CO_2 also occurs. Therefore, the obtained selectivities were calculated and plotted in Figure 3 as a function of the corresponding conversion values.

Figure 3

In both cases, the selectivity decreases with the increment of the CO conversion and this behavior may be related to different phenomena that are occurring simultaneously.

Firstly, it has to be remarked that the conversion was increased with the reaction temperature, and these results could be explained in part, by the higher activation energy of CO_2 methanation, a probable collateral and undesired process due to the presence of CO_2 in the feed-stream that became more determinant with the temperature [4]. However, the availability of CO and CO_2 can be strongly marked by the occurrence of the WGS equilibrium reaction. Garbis et al. [4] suggested in their kinetic study of selective methanation of CO over $Ru/\gamma-Al_2O_3$ catalysts that the CO_2 can be directly converted into methane, thus the indirect route via R-WGS followed by the subsequent CO methanation could be excluded. In our case, a more in-depth study is required to establish the reaction intermediates as the temperature increases and to analyze which processes contribute and in what proportion.

Which is evident is that the monolith with the lowest catalytic layer thickness (~2 μm) exhibits a superior selectivity at CO conversions below 95%, whose are achieved at temperatures below 200 ºC. This superior performance result may be related with the catalytic layer thickness achieved with the two analyzed CAT loadings, since this parameter strongly influences transport phenomena during the catalytic reaction. In fact, similar results of higher performances achieved with low amounts of loaded catalyst, which means lower catalytic layer thickness, have been observed in previous studies of structured catalysts involved in exothermic reactions such as the CO oxidation [25] or the CO_2 methanation [26]. In our case, the fact that for both monoliths the space velocity is constant means that the total flow of the feed-stream in the case of the 1.0 mg/cm^2 loading is twice respect to that used for the 0.5 mg/cm^2 one. However, the volume of both micromonoliths is the same so two different volumetric flow rates and consequently different linear gas velocities were used for the same volume of reactor (monolith).

Therefore, when comparing these two monoliths under these conditions, we are varying the linear velocity of the gases that controls external diffusion and the thickness of the

catalytic layer that controls internal diffusion. Under such conditions we cannot discriminate which is relevant to explain the observed differences in CO conversion and selectivity in hydrogen consumption. This hypothesis is not analyzed in most studies presented up to now about CO methanation catalysts [4, 5, 27]. However, this would require further experimental work in order to quantify such effect and to establish if these are mass or heat transport phenomena.

Moreover, indirectly, the catalytic results presented in Figures 2 and 3, make it possible to select the temperatures of 180 and 200 ºC, as temperatures in which a compromise between the suggested H_2 consumption values and CO conversion values close to minimum CO emissions <20 ppm are achieved. This temperature range was selected to study the effect of the modification of the other parameters, as can be confirmed in Table 2.

3.1.2. Effect of the space velocity: For the analysis of different space velocities, M2, M3 and M9-M14 experiments were performed (see Table 2) and the CO conversion as well as the H_2 consumption at 180 and 200 ºC are presented in Figure 4. In addition, the selectivity values plotted as a function of the corresponding CO conversion are presented in Figure 5.

Figure 4

Figure 5

Firstly, it is observable that the CO conversion (Figure 4A) decreases with the increment of the space velocity, which is a behavior observed by other authors in their studies about the influence of such parameter in the CO methanation process, even with different catalysts such as Co-Fe bimetallic [27] systems or $NiO-La_2O_3-MgO/Al_2O_3$ [14]. This expectable behavior is mainly produced by the decrease of the residence time as the

space velocity increases. Moreover, only for the lowest space velocity studied (0.667 $m^3/[kg \cdot s]$), the CO conversion is almost complete (Figure 4A).

The superior performances in CO conversion are achieved at 200 ºC with a less pronounced decreasing trend. The discrepancy in trends at 180 and 200 ºC may be related to a lowering of the rate of the CO consumption process in the case of the experiment carried out at 180 ºC respect to that of the experiment at 200 ºC [4]. Despite this, the evaluated temperatures generate high conversion values that, together with the exothermic nature of CO methanation, could be generating mass and/or heat transport phenomena, which would also influence these results. Taking into account that the thickness of the catalytic layer is relatively low in the studied micromonolith (~2 μm), it is probable that the external mass transfer phenomena may be less decisive or even insignificant, as we have observed in previous studies over microreactors with catalytic layer thicknesses below 20 μm used in the preferential oxidation of CO in the presence of H_2, where mass transfer limitations were discarded [25]. However, it has to be remarked that further experiments are required to verify this in our case.

Regarding the H_2 consumption (Figure 4B), the results follow an expected trend in line with those of the CO conversion. Less H_2 consumption is observed as the space velocity increases. In addition, if the experiments carried out at 180 ºC present lower CO conversion, no superior H_2 consumption could be expected as occurred indeed. Finally, in the case of the selectivity (Figure 5), an opposite behavior is observed, because as higher the space velocity higher the selectivity. Nevertheless, the experiments carried out at 200 ºC presented lower selectivity values than those generated at 180 ºC.

According to the results presented in Figures 4 and 5, within the space velocities analyzed, the value of 0.667 $m^3/[kg \cdot s]$ allows obtaining the most suitable performance

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for the monolith with the lowest loading of CAT, in terms of CO conversion, but selectivity is sacrificed to some extent.

3.1.3. Effect of the CO content in the feed-stream:
In a fuel processor that integrates different units, including the methanation unit, there may be fluctuations in the composition of the input to each of them. Therefore, it is important to analyze the response to possible fluctuations, for example, of CO, which is one of the key components in the feed of a methanation unit. Therefore, the effect of the CO content in the feed-stream on the CO conversion and the H_2 consumption was tested, and the results are presented in Figure 6.

Figure 6

The CO conversion (Figure 6A) decreases with the increment of the CO content and such decrease is more pronounced in the experiments carried out at 180 ⁰C. These results are in agreement with that reported by Garbis et al. [4] in their study of kinetic and designs aspects of CO methanation over $Ru/\gamma-Al_2O_3$ catalysts, where two CO contents were tested (5000 and 14100 ppm) and the higher one generated less CO conversion. However, results interesting that in such study, the loss of conversion due to the increment of CO content is around 30% at 180 ⁰C and 70% at 200 ⁰C while for our structured catalysts the loss of activity does not reach 0.5% or 2% at 180 and 200 ⁰C respectively (Figure 6A).

These authors also pointed out that although the increase in the CO content decreases the conversion, it also reduces the negative effect of mass transfer phenomena due to the diffusion of CO in the pores [4]. Therefore, the lower loss of CO conversion in our case, could also indicate a better mass transfer in the process, thanks to the structuring of CAT. However, this must be confirmed with a comprehensive kinetic study, which

allows evaluating the effectiveness factor with respect to CO concentration. On the other hand, as for the H_2 consumption trends, that of the experiments carried out at 200 ºC is higher, although in both cases (180 ºC and 200 ºC) the values appear constant against the change in the CO feed. ==This behavior again has to be related to the manifestation of collateral reactions such as CO_2 methanation or the R-WGS reaction cited above, in which the main components of the reaction (H_2, CO and CO_2) are involved, because their effects are evident, although Complementary studies are needed to know in what proportion these collateral reactions contribute.==

3.1.4. Effect of the H_2 content in the feed-stream: As in the case of CO, H_2 is another key component of the process and its content in the reaction mixture can fluctuate too if the methanation unit is integrated within a reformer. Therefore, it is also pertinent to evaluate possible effects of such fluctuation on the catalytic performance of structured systems. But in this case, the fluctuation of H_2 is evaluated in reactive streams with two CO contents (250 and 1200 ppm) which are the concentrations of the extremes in the range evaluated during the analysis of the fluctuation of the CO content. In this sense, the catalytic results of CO conversion and H_2 consumption depending on H_2 feed for the feed-streams with 250 and 1200 ppm of CO ==are presented in Figure 7==.

Figure 7

The CO conversion for the feed-stream with 250 ppm of ==CO (Figure 7A)==, does not present appreciable differences with the increment of the of the H_2 content due to the fact that as for the experiments at 180 ºC as for those at 200 ºC, the conversion is almost 100%. While for the case of the experiments with 1200 ppm of CO, the increment of H_2 content in the feed-stream results in the enhancement of the CO conversion. This means that the lower catalytic activity produced by the increment of CO, observed in Figure 6A, is compensated by the inclusion of H_2.

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Similar results were observed by He et al. [14] in their study of the influence of the H_2/CO ratio in the feed-stream during CO methanation using $NiO-La_2O_3-MgO/Al_2O_3$ catalysts. They also confirmed the enhancement of the CO conversion due to the increment of the H_2 content in the feed-stream. However, such enhancement is more evident as the CO content increased, which would agree with the fact that the experiments carried out with 1200 ppm of CO presented a superior effect of the increment of H_2 (Figure 7C) than those of 250 ppm of CO (Figure 7A). What is clear is that the higher the H_2 content, the more methane production can be favored.

3.1.5. Evaluation of catalytic activity after tests modifying different variables:

Considering that the experiments M1-M4 and M9-M28 (see Table 2) were performed over the same micromonolith, loaded with 0.5 mg/cm^2, it is important to verify if after all of these experiments, some modifications of its catalytic performance are observable. Therefore, the spent micromonoliths were recovered after M1 and M3 tests and further used in additional tests, under similar experimental conditions, to assess their performance without regeneration and the results of CO conversion and H_2 consumption are presented in Figure 8.

Figure 8

Surprisingly, there is no loss of performance. On the contrary, a slight increase is observed in the conversion of CO (Figure 8A), combined with a lower H_2 consumption (Figure 8B). This is a positive result on the performance of the catalyst studied in this paper, although it requires a much more in-depth study to establish the possible causes of the observed stability. However, this may be related to parameters of both the active phase (Ru particles) and the support (TiO_2), as established by Abdel-Mageed et al. [5] in a study on the role and influence of metal-support interactions in Ru/TiO_2 catalysts for

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the methanation of CO. These authors observed that, although a high dispersion of the active Ru species is key, the specific area and the porous structure of the support can also influence.

3.1.6. Long-term stability and shut-down/start-up tests of the structured CAT

The results of the long-term catalytic activity tests are presented in Figure 9.

Figure 9

The micromonolith shows stable activity (both CO conversion and H_2 consumption) throughout the evaluation period and no effect of the shut-down/start-up processes is observed. This is a positive result on the performance of this structured catalytic system and lays the groundwork for further development of a promising system for CO methanation. In literature, the study of the structuring of this type of catalyst is practically non-existent, and even less there are reports of such long stability studies. Zhang et al. [28] are some of the few authors who report the study of long-term catalytic activity test (100 h) of a powder catalyst (La_2O_3 promoted Ni/Al_2O_3 catalysts). Their results are promising too although they do not include the shut-down/start-up processes, whose are quite demanding for the catalyst because they subject them to cooling and heating cycles that could affect both the dispersion of the active phase and the textural properties of the support. However, this does not seem to happen in our case and this may indicate a very good interaction between the active phase and the support that allow us to carry out this type of long test.

Other possible source of deactivation in methanation catalysts is usually the formation of carbonaceous deposits, although it has been observed that H_2O may act as a promoter of the gasification of the carbon that is deposited in this type of catalysts [29, 30]. Despite this, further experimental work would be required for analyzing the spent

As mentioned above, the shut-down/start-up cycles can generate drastic changes in the catalysts, mainly due to temperature shocks. For this reason, it is intended to explore the possible influence of the application of a series of those cycles continuously on the micromonolith already tested for 340 h. Therefore, the next steps were followed during every shut-down/start-up cycle: a) cooling of the reactor from 180 ºC to 50 ºC in N_2 stream. b) 2 h in N_2 stream at 50 ºC. c) Heating of the reactor until 180 ºC (5 ºC/min) and change in the N_2 feed by mixture of reaction; 4) Once the temperature is reached (180 ºC), measurement of the CO conversion. The results are presented in Figure 9B.

The micromonolith again shows its considerable stability, since after 340 hours of operation, it is capable of withstanding 10 additional shut-down/start-up cycles during an extra analysis period of 35 hours, for a total of 375 hours of operation. There are no changes in activity (CO conversion or H_2 consumption), which once again confirms that the results obtained in the studies of different variables (Table 2) are reliable. In addition, the resistance of the structured catalyst to the shut-down/start-up cycles shows its versatility in an application in which discontinuous production scenarios can occur.

4.   Concluding Remarks

The viability of structuring a Ru/TiO_2 powder catalyst by means of the washcoating method and using metal micromonoliths was successfully carried out in the present study. Therefore, micromonoliths with different catalyst loading were achieved through an optimized and reproducible procedure.

In addition, the different structured devices showed suitable catalytic performances in the selective methanation reaction, comparable with other powder catalysts presented

in previous studies. Therefore, this is a remarkable result of the present work since it is the first time that the cited Ru/TiO_2 catalyst tested as a structured catalyst in the selective CO methanation. Moreover, it confirms that the structuring process does not vanish the catalytic abilities of the Ru/TiO_2 system.

Regarding the modification of different parameters during the catalytic tests, firstly it was observed that the system with the lowest specific loading of catalyst (0.5 mg/cm2) presented the highest performance, while for the temperature of reaction, the better results were obtained at intermediate values (180 and 200 ºC), where a suitable balance between CO conversion and H_2 consumption was achieved.

The modification of the space velocity showed that lowest tested values generated better results, which demonstrated the influence of the residence times during the catalytic reaction. As for the CO and H_2 contents in in the feed-stream, these generate an opposite effect. For one hand, as higher the amount of CO fed lower the CO conversion, and on the other hand, as higher the amount of H_2 higher the CO conversion.

Finally, another important result is the considerable catalytic stability demonstrated by the structured system that was evaluated for more than 350 h, including cycles. This not only shows that the catalyst can be structured effectively, and analyzed in reaction, but it can also demonstrate benefits that make it interesting to develop future more advanced structured systems based on the protocols described in the present study. In the same way, this type of structure has demonstrated its reliability to carry out studies that allow the development of kinetic models based on its catalytic performance in future work.

5.   Acknowledgements

6.   References

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TABLES

Table 1. Optimized formulation of the slurry of CAT for the washcoating of metal micromoliths*

Component	Weight Percentage (wt.%)
CAT	5.03
Colloidal alumina	1.00**
PVOH	1.94
H_2O	92.03

* The pH of the slurry was adjusted to 4 with diluted HNO_3.
** This wt.% corresponds to the colloidal alumina contained in the used Nyacol® AL20 (20 wt.% alumina in water).

Table 2. Experiments carried out over the structured micromoliths*

Modified variable	Marker	Specific CAT loading ** (mg/cm²)	Cat. layer thickness ε*** (µm)	Temp. (°C)	Space Velocity (m³/[kg·s])	CO concentration (ppm)	H₂ concentration (Vol.%)
Loading of CAT	M1	0.5	~2	160	1.333	500	60
	M2			180			
	M3			200			
	M4			300			
	M5	1.0	~4	160			
	M6			180			
	M7			200			
	M8			300			
Space Velocity	M9	0.5	~2	180	0.667	500	60
	M2				1.333		
	M10				2.000		
	M11				2.667		
	M12			200	0.667		
	M3				1.333		
	M13				2.000		
	M14				2.667		
CO Feed	M15	0.5	~2	180	0.667	250	60
	M2					500	
	M16					800	
	M17					1200	
	M18			200		250	
	M3					500	
	M19					800	
	M20					1200	
H₂ Feed	M21	0.5	~2	180	0.667	250	40
	M22						50
	M2						60
	M23			200			40
	M24						50
	M3						60
	M25			180	2.667	1200	40
	M26						50
	M17						60
	M27			200			40
	M28						50
	M20						60

* Components that present constant Vol.% in all the experiments: CO_2 Vol.% = 15%; H_2O Vol.% = 15. N_2 was used for balance.

** Specific CAT loading represented as the CAT weight loaded divided by the geometric area of the micromolith (420 cm²).

*** Catalytic layer thickness was calculated as $\varepsilon = \frac{Wcat}{\rho_{cat} \times S_g}$, where W_{cat} is the catalytic load (216 or 440 mg), S_g is the geometric surface of the used micromoliths, and ρ_{cat} is the catalyst density (4.11 g/cm³) calculated for a matrix Ru (8.3 wt.%), TiO_2 (75.1 wt.%) and Al_2O_3 (16.6 wt.%).

FIGURE CAPTIONS

Figure 1. Particle size distribution and zeta potential of CAT

Figure 2. Catalytic performance of two different loadings of CAT in the structured micromonoliths [Constant Parameters: Space velocity: 1.333 m^3/[kg·s]; CO concentration: 500 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15]: A) CO conversion; B) H_2 consumption.

Figure 3. Effect of the loading of CAT over the selectivity to CO methanation [Constant Parameters: Space velocity: 1.333 m^3/[kg·s]; CO concentration: 500 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15]

Figure 4. Effect of the space velocity [Constant Parameters: Loading of CAT: 0.5 mg/cm^2; CO concentration: 500 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15]: A) CO Conversion; B) H_2 consumption

Figure 5. Effect of the space velocity over the selectivity to CO methanation [Constant Parameters: Loading of CAT: 0.5 mg/cm^2; CO concentration: 500 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15]

Figure 6. Effect of the CO content in the feed-stream [Constant Parameters: Loading of CAT: 0.5 mg/cm^2; Space velocity: 0.667 m^3/[kg·s]; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15]: A) CO conversion; B) H_2 consumption

Figure 7. Effect of the H_2 content in the feed-stream [Constant Parameters: Loading of CAT: 0.5 mg/cm^2;; CO_2 Vol.% = 15; H_2O Vol.% = 15] / A) CO conversion for CO feed 250 ppm; B) H_2 consumption for CO feed 250 ppm; C) CO conversion for CO feed 1200 ppm; D) H_2 consumption for CO feed 1200 ppm

Figure 8. Evaluation of catalytic activity after the different tests to which the micromonolith has been subjected [Constant Parameters: Space velocity: 1.333 m^3/[kg·s]; Loading of CAT: 0.5 mg/cm^2; CO concentration: 500 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 15; H_2O Vol.% = 15] : A) CO conversion; B) H_2 consumption

Figure 9. A) Long-term catalytic stability evaluation [Constant Parameters: Temperature: 180 ºC; Space velocity: 1.333 m^3/[kg·s]; Loading of CAT: 0.5 mg/cm^2; CO concentration: 300 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 21; H_2O Vol.% = 16]; B) Shut-down/Start-up test [Constant Parameters: Temperature: 180 ºC; Space velocity: 1.333 m^3/[kg·s]; Loading of CAT: 0.5 mg/cm^2; CO concentration: 300 ppm; H_2 Vol.% = 60; CO_2 Vol.% = 21; H_2O Vol.% = 16]
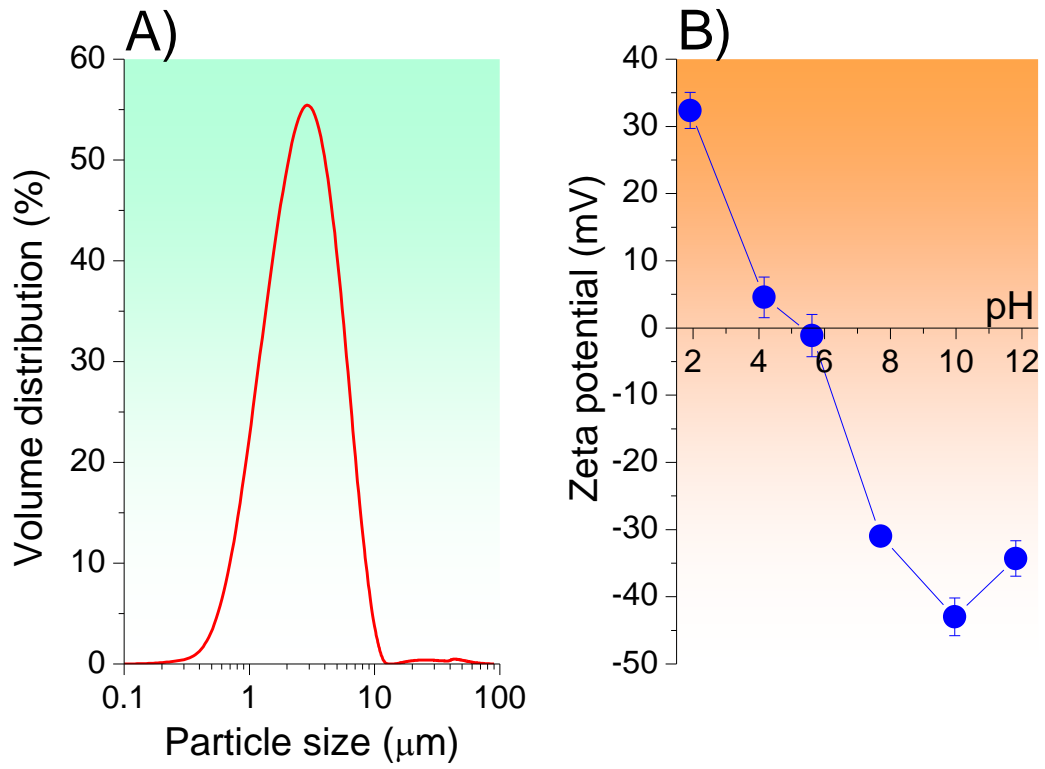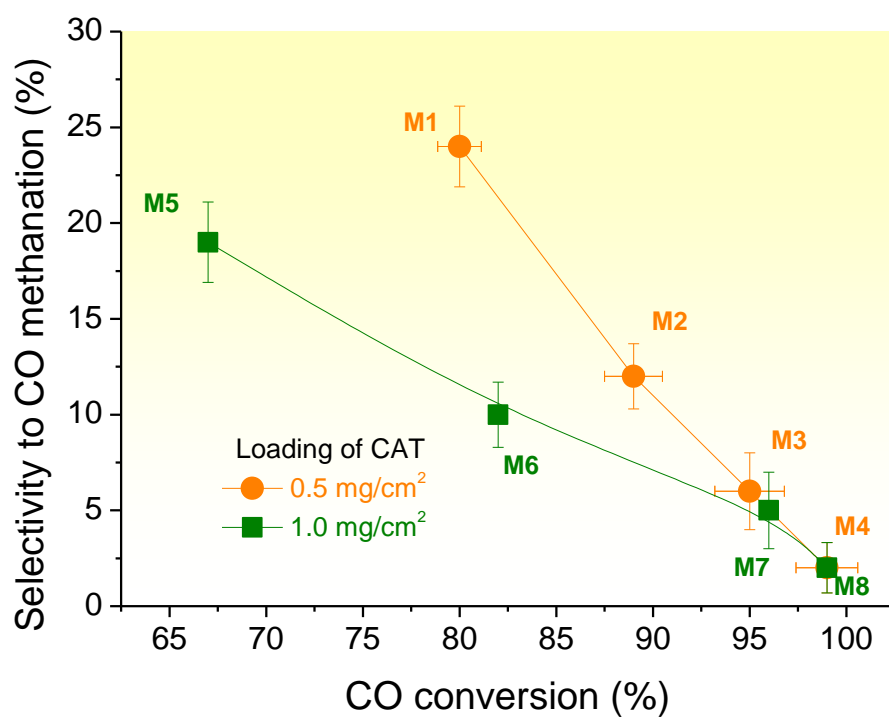
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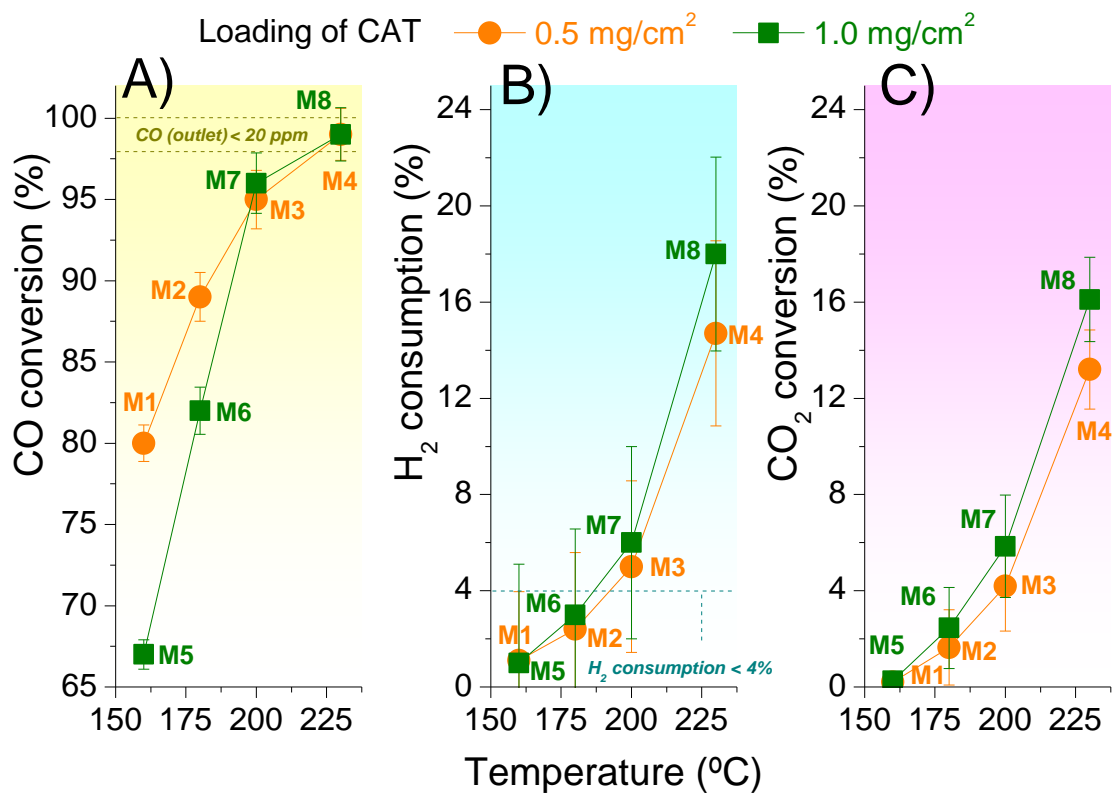
FIGURE 2

FIGURE 3
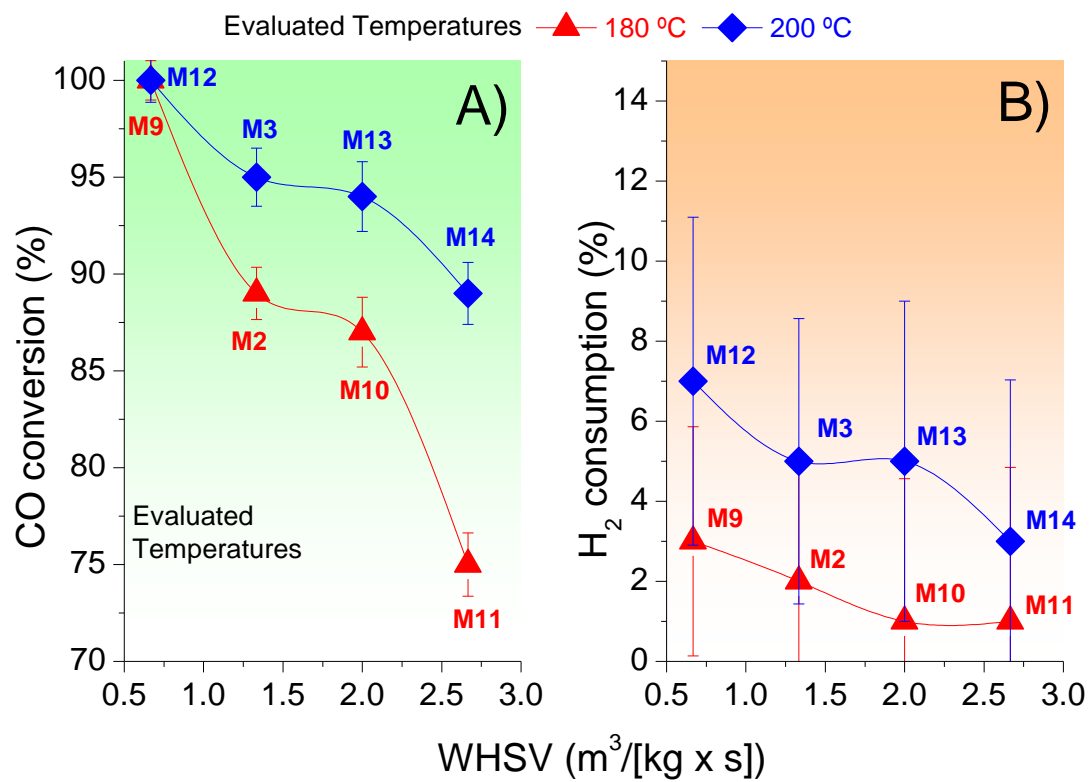
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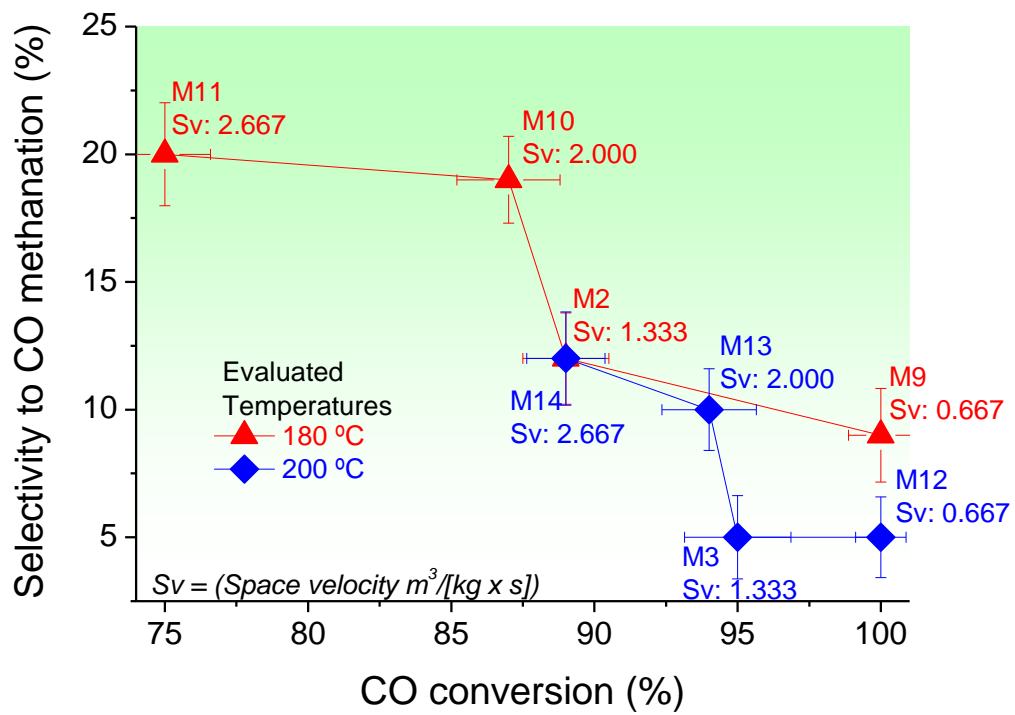
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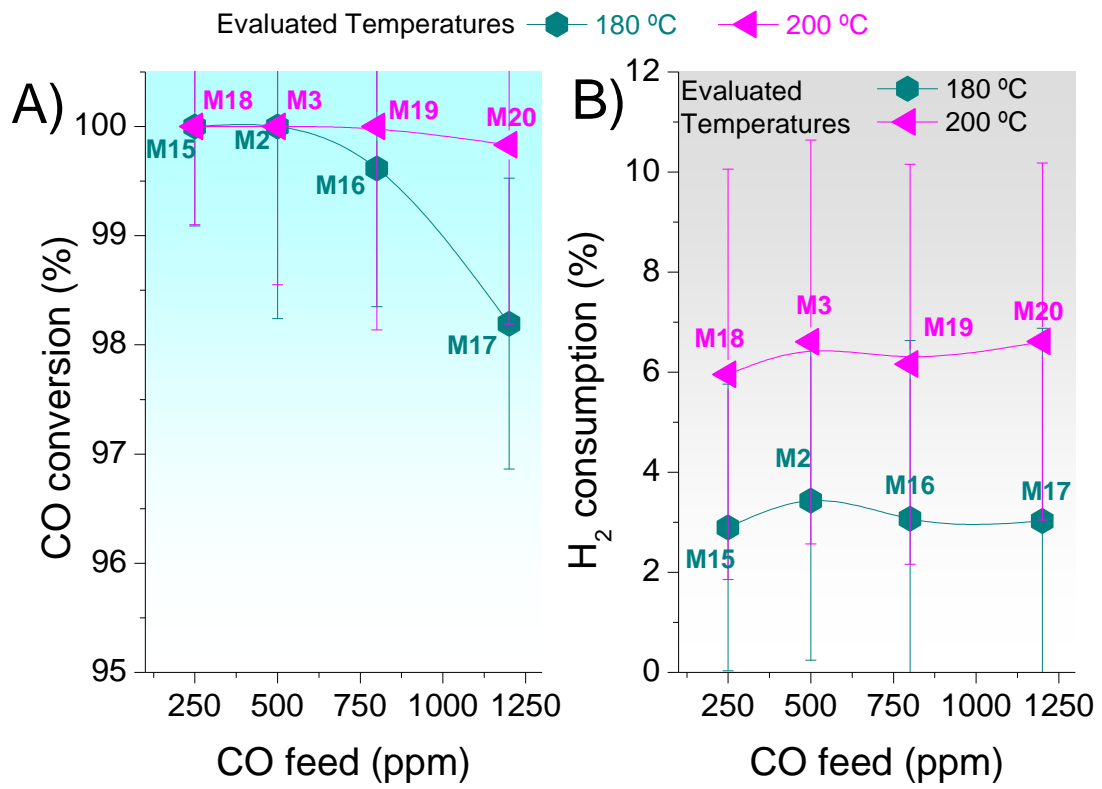
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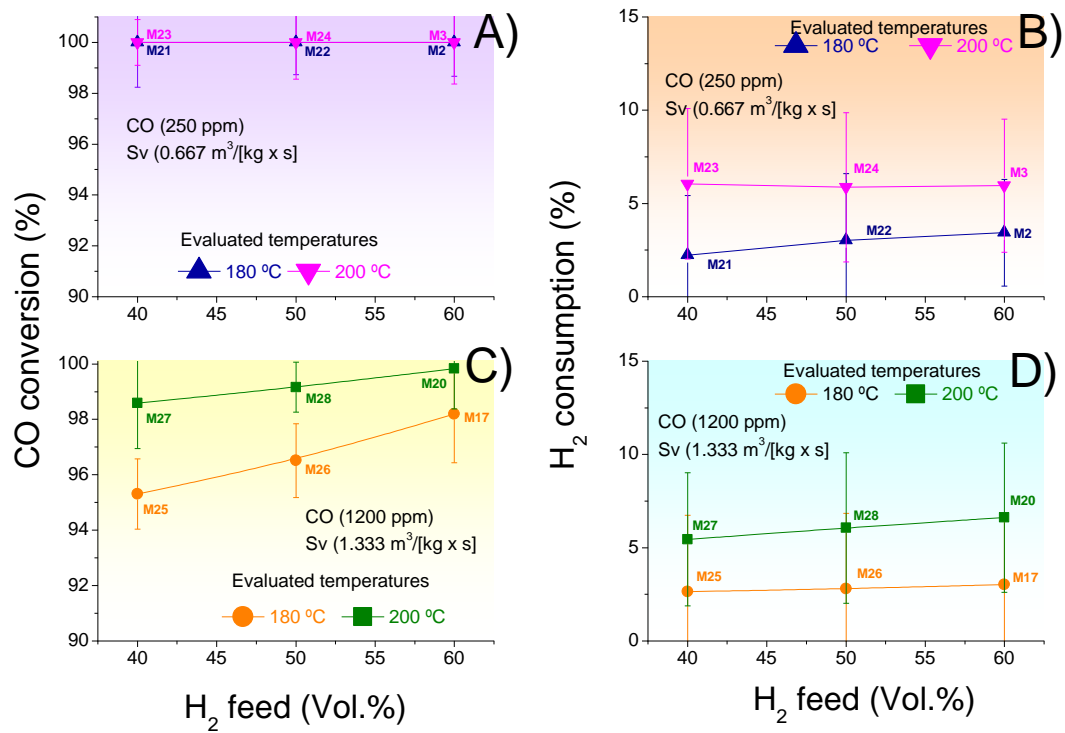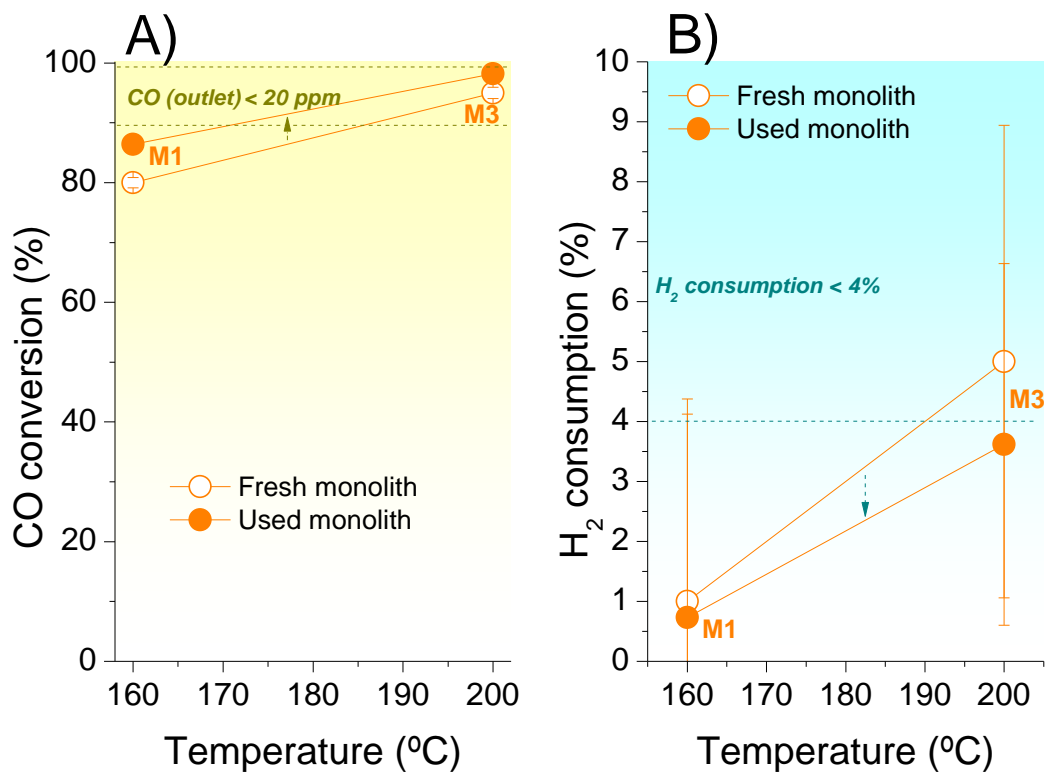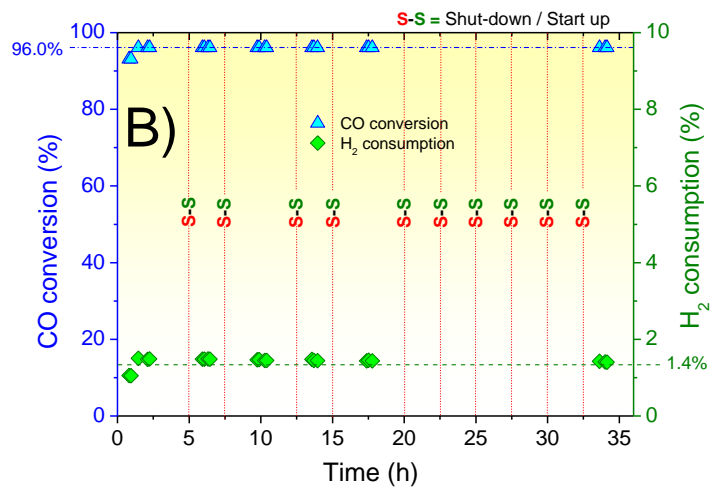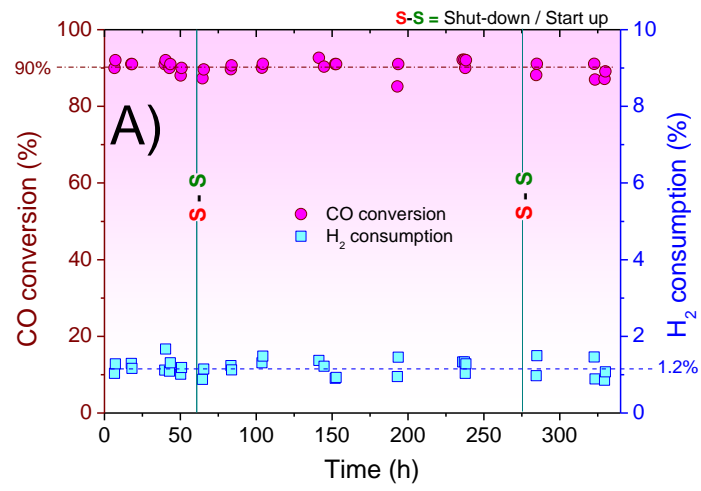
FIGURE 7

FIGURE 8

FIGURE 9

Credit Author Statement

Metal micromonoliths for the cleaning of H₂ by means of methanation reactions

O.H. Laguna: *Methodology, Investigation, Formal Analysis, Writing-review and editing;* **A. Muñoz-Murillo:** *Methodology, Investigation;* **L.F. Bobadilla:** *Methodology, Investigation, Formal Analysis*; **L.M. Martínez T:** *Investigation, Formal Analysis;* **M. Montes:** *Supervision, Resources, Writing-review and editing;* **M.A. Centeno:** *Supervision, Visualization, Writing-review and editing;* **J.A. Odriozola:** *Project administration, Funding acquisition*

Metal micromonoliths for the cleaning of H₂ by means of methanation reactions

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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.

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