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Capillary microreactors based on hierarchical SiO₂ monoliths incorporating noble metal nanoparticles for the Preferential Oxidation of CO

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Novel hierarchical SiO₂ monolithic microreactors loaded with either Pd or Pt nanoparticles have been prepared in fused silica capillaries and tested in the Preferential Oxidation of CO (PrOx) reaction. Pd and Pt nanoparticles were prepared by the reduction by solvent method and the support used was a mesoporous SiO₂ monolith prepared by a well-established sol-gel methodology. Comparison of the activity with an equivalent powder catalyst indicated that the microreactors show an enhanced catalytic behaviour (both in terms of CO conversion and selectivity) due to the superior mass and heat transfer processes that take place inside the microchannel. TOF values at low CO conversions have been found to be ~2.5 times higher in the microreactors than in the powder catalyst and the residence time seems to have a noticeable influence over the selectivity of the catalysts designed for this reaction. The Pd and Pt flexible microreactors developed in this work have proven to be effective for the CO oxidation reaction both in the presence and absence of H₂, standing out as a very interesting and

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suitable option for the development of CO purification systems of small dimensions for portable and on-board applications.

Keywords: Noble metal nanoparticles, mesoporous SiO₂, capillary microreactors, hierarchical monoliths, Preferential Oxidation of CO (PrOx CO).

1. Introduction.

Due to the steep rise in environmental pollution, in the last few years new policies of sustainability are being encouraged in order to boost renewable energies usage and the development of cleaner technologies and industrial processes [1]. In this context, polymer electrolyte membrane (PEM) fuel cells stand out as a clean and efficient way to obtain energy directly from the chemical reaction between H₂ and O₂, both in large scale but also in smaller scale applications, such as portable devices, substituting the traditional Li-ion batteries. Micro fuel cells are preferred to traditional Li-ion batteries since they provide a higher energy density and can therefore serve as micro-power sources for certain systems [2]. However, these devices require the catalytic treatment of the H₂ streams to deliver them with sufficient purity to the fuel cell. This treatment involves, among other steps, the selective oxidation of CO (also referred to as Preferential Oxidation of CO or PrOx in the literature) which is mandatory to comply with the H₂ purity levels required in a fuel cell (CO concentration level <10 ppm). Microreactors are both an interesting and viable option for this operation in miniaturized PEMFC. Microreactors, in addition to their small size, also present several advantages with respect to packed-bed reactors, such as large surface-to-volume ratios which lead to optimized heat and mass transfer processes that reflect in process

intensification as well as the ability to be incorporated in complex, non-conventional reactor architectures including very small reaction units. Furthermore, as a consequence of the small size of the channels, the radial diffusion time in the gas phase is very short, helping avoid the formation of unwanted by-products and improving temperature control significantly. These systems also display a faster response time, lower pressure drop and higher ease in integration and safety in operation than typical particulate catalysts, as it has been stated for different wall coated microreactors for methanol steam reforming [3] and selective oxidation processes [4]. For all these reasons microreactors are very promising candidates for their application in H₂ purification processes (in the PrOx reaction) for portable fuel cell and micro fuel cell applications, as we postulate in this work.

Different catalytic systems have been developed and tested in the PrOx reaction. Nowadays, it is widely accepted that platinum group metals deposited over inorganic supports (with and without promoters) perform very well under realistic conditions in the appropriate range of temperatures for this reaction [5],[6]. Our group recently reported that palladium-based catalysts can be interesting for their application in the preferential oxidation of CO [7,8].

There are several microreactor configurations that have been successfully developed for the PrOx reaction, including micromonoliths, silicon chips and metal foils [9]-[11]. Usually, the microreactors designed for this application consist on thin layers of catalyst deposited on these structures [4],[12],[13]. However, the preparation of mechanically stable, homogeneous crack-free coatings of the catalyst along the microchannel is not straightforward. In this sense, the preparation of the catalyst bed as a continuous porous monolith along the channels poses an advantage from a synthetic point of view, due to the high reliability and robustness of the synthetic procedures. Since the PrOx reaction

is a gas-solid catalytic system, distribution of the catalytic active phase in a highly porous structure that favours the gas-catalyst contact also involves an enhanced catalytic behaviour of the system. The microreactor systems have shown to perform very successfully in several applications, including other gas-solid reactions [5],[14],[15]. For these reasons, we undertook the preparation of flexible capillary microreactors for the PrOx reaction in small devices, where the active phase consists on noble metal nanoparticles (Pd or Pt) deposited on a hierarchical porous SiO₂ structure. In this sense, SiO₂ based materials present very interesting properties and can be synthesized as single or mixed oxides to improve its performance (due to a synergetic effect) in a variety of applications [16][17][18]. These microreactors have been evaluated in the PrOx reaction and proved to perform effectively under the desired conditions displaying also a good long-term activity in CO oxidation in the absence of H₂.

2. Materials and methods.

2.1. Synthesis and purification of the metal nanoparticles.

Palladium and platinum nanoparticles were synthesized by the reduction-by-solvent method under an inert atmosphere, according to a previously published procedure [7],[8],[19]. Briefly, the metal precursors were dissolved in an alcohol solution containing a polymer (PVP, poly-*n*-vinylpyrrolidone) that acts as surfactant and avoids sintering of the metal nanoparticles once generated. The nanoparticles were synthesized by thermal treatment of the solution and stable colloids were obtained. Purification of the resulting nanoparticles resulted in suspensions of known final metallic concentration

of the ready-to-use colloids. Impregnation of the samples was performed immediately after purification of the nanoparticles.

2.2. Synthesis of the mesoporous SiO₂ monoliths.

Mesoporous SiO₂ monoliths were prepared inside fused silica capillaries by a sol-gel methodology, adapting an already published procedure [20],[21]. The silica capillaries used in the synthesis are 20 cm long, have an inner diameter of 0.25 mm and were purchased from Varian. Before the synthesis, the capillaries were activated by flowing a 1M solution of NaOH through them, sealing their endings and heating them at 40°C for 3 h. After that, the capillaries were rinsed with glacial acetic acid followed by H₂O to rinse the capillary.

The SiO₂ precursor solution was prepared by dissolving 1.054 g polyethylene glycol (PEG) (10K, Sigma Aldrich) and 1.081 g urea in 12 g of acetic acid (0.01M). The solution was moved to an ice bath and 4.81 g of tetramethyl orthosilicate (TMOS) were then added dropwise to form a very viscous transparent solution that was kept under vigorous stirring at 0°C for 40 minutes.

To prepare the SiO₂ monoliths, this solution is flowed through the capillaries by means of a vacuum pump. Once the capillaries were filled with the precursor solution, they were sealed and the gels were aged by submitting the samples to a thermal treatment of 40°C overnight and 120°C for 3 h. At 120°C, the urea is known to decompose generating ammonia and this process is responsible for the formation of mesopores, as other authors have reported [21]. A final calcination step was performed under vacuum at 300°C for 24 h (heating rate of 3°C/min) in order to remove the surfactant, with this decomposition being responsible for the formation of the macroporous structure of the

monoliths. This calcination procedure has been reported to be effective for the total decomposition of the surfactant from the silica structure [20]. Since the Si precursor concentration in the solution prepared is perfectly known, it is possible to estimate the amount of SiO₂ generated inside the capillaries just from the volume of solution filling the capillary, assuming complete gelation of the Si precursor and total removal of the surfactant.

Powder mesoporous SiO₂ has also been prepared from the abovementioned solution. For the preparation, the gel was introduced in cylindrical containers (1.5 cm inner diameter) and submitted to the same thermal treatment as the capillaries. After the vacuum calcination the macromonoliths obtained were crushed to a fine powder, which was used as catalyst support and for characterization purposes.

2.3. Preparation of the capillary microreactors.

The mesoporous SiO₂ monoliths were loaded with the metal nanoparticles (Pd or Pt) by impregnation. In order to deposit the nanoparticles onto the SiO₂ structure, the appropriate amount of metal suspension was evaporated and the dry Pd or Pt nanoparticles were redispersed in the same volume of methanol corresponding to the capillary volume. By this procedure, the metal suspension is flowed through the capillary and the particles remain within the capillary, dispersed on the SiO₂ monolith.

As a final step, the capillaries were dried at 150°C for 4 h to ensure complete removal of the methanol solvent. Microreactors with a nominal metal loading of 1.5 wt% metal have been prepared in this work. An equivalent powder catalyst (Pd/SiO₂) was also prepared by the wet impregnation method, as described elsewhere [7]. For this synthesis, the appropriate amount of metal nanoparticles (to yield 1 wt% of metal

loading) was stirred with 1 g of powder mesoporous SiO₂ (10K) for 48 h at room temperature. After that, the solvent was evaporated and the catalyst was dried at 60°C and ground to a fine powder.

2.4. Characterization of the samples.

The metal nanoparticles were characterized by transmission electron microscopy (TEM, JEOL-2010) in order to analyze the average particle size and particle size distribution, by counting a minimum of 100 particles in each case, as explained in our previous work [19]. Due to the spherical shape of the nanoparticles, the metal dispersion (*D*) of the nanoparticles on the supports can also be estimated from the particle size (*d*) with the following approximation [22]:

$$D \approx 0.9/d(\text{nm})$$

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to analyze the real metal loading of the microreactors and the powder catalyst. For the powder catalyst, a certain amount of sample was extracted with 2 ml of aqua regia for 48 h at room temperature. The sample was filtered and the liquid phase recovered and diluted to 25 ml with deionized water. For the microreactors, a section of capillary was cut into smaller pieces and mixed with 0.5 ml of aqua regia. After the metal extraction, the samples were filtered and the liquid phase recovered with a known volume of deionized water. The metal concentration of the samples was calculated by comparing the results with calibrated standards prepared with the same acid matrix.

The textural characterization of the powder SiO₂ samples was carried out by means of adsorption of N₂ at -196°C and CO₂ at 0°C (Autosorb 6, Quantachrome). Before the adsorption measurements the samples were outgassed *in situ* under vacuum at 250°C for 4 h in order to remove adsorbed impurities. Apparent surface area values were calculated from nitrogen adsorption isotherms using the BET equation (S_{BET}). Total micropore volume ($V_{\text{DR}}(\text{N}_2)$) and narrow micropore volume ($V_{\text{DR}}(\text{CO}_2)$) were calculated applying the Dubinin–Radushkevich (DR) equation to the N₂ adsorption data at -196°C and the CO₂ adsorption data at 0°C, respectively [23],[24]. The mesopore size distributions were calculated by applying the Barrett–Joyner–Halenda (BJH) method to the isotherms desorption branch [25]. The mesopore volume ($V_{\text{meso N}_2}$) was calculated from the N₂ isotherm considering the volume adsorbed between the partial pressures 0.9 and 0.2 in the desorption branch.

The morphology, texture and homogeneity of the Pd/SiO₂ monoliths was assessed by the analysis of different sections of the samples by optical microscopy and scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDX, Hitachi S3000N). Elemental mapping was also performed on these samples in order to analyze the metal distribution on the monoliths.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the microreactors before and after the catalytic tests, by using a VG-Microtech Multilab 3000 spectrometer equipped with a Mg K α X-ray source and an analyzer adjusted at 50eV pass energy. Further calibration was made with respect to the C 1s peak of carbon at 284.6 eV.

2.5. Catalytic tests.

The microreactors activity in the PrOx reaction was evaluated under non-isothermal conditions at a heating rate of 2°C/min with a gas feed composition of 2% CO, 2% O₂, 30% H₂ in He and a total gas flow of 5 ml/min ($\lambda=2 \cdot ([O_2]/[CO])$, in this case $\lambda=2$). In some cases, gas flow rates of 1.25, 2.5 and 7.5 ml/min were also used in order to adjust the space velocity within the reactor. The powder catalyst was tested under the same conditions, using a U-shaped quartz reactor with 100 mg of sample and a gas flow of 100 ml/min. Prior to the reactions, all the samples underwent a reducing treatment which was carried out under 10% H₂ in He at 200°C for 2 h (heating rate 5°C/min). Isothermal experiments at the same flow rates were conducted in some cases. Experiments in the absence of H₂ were also performed for some samples with a gas feed composed of 1% CO, 20% O₂ in He and a gas flow of 5 ml/min. In these cases the samples were submitted to the same thermal treatment described above prior to reaction, in a gas stream containing 10% O₂ in He.

The performance of the samples was evaluated by analyzing the gas composition exiting the reactor with a GC chromatograph (Agilent 6890N) working with a CTR-I column (Alltech) operating at 80°C and a TCD detector. The parameters used to assess the catalysts behaviour were CO conversion, O₂ conversion and selectivity (towards CO oxidation), which were calculated as follows:

$$Conv.CO(\%) = \frac{[CO]_0 - [CO]}{[CO]_0} \cdot 100$$

$$Conv.O_2(\%) = \frac{[O_2]_0 - [O_2]}{[O_2]_0} \cdot 100$$

$$Selectivity(\%) = \frac{[CO]_0 - [CO]}{[O_2]_0 - [O_2]} \cdot 50$$

The space velocity (GHSV, $\text{ml h}^{-1} \text{g}^{-1}$) was calculated from the amount of catalyst and the gas flow rate used in each experiment. The Turn Over Frequency (TOF, s^{-1}), defined as the amount of CO converted per mol of surface metal, was also used as a parameter to evaluate the performance of the samples.

3. Results and discussion.

3.1. Nanoparticles characterization.

Previous works carried out by our group have shown that metal nanoparticles synthesized by the reduction-by-solvent method display a very small particle size and very narrow particle size distribution [19]. Figure S1 shows the TEM images of the Pd and Pt nanoparticles prepared for this work and the histograms showing the particle size distributions. As it can be observed, highly stable metallic colloids are obtained by this method, with nanoparticles smaller than 4 nm (average size) in both cases that are very well dispersed in the suspension and stable against sintering. The long-term stability of the metallic colloids prepared by this methodology has been widely stated in the literature [26].

3.2. Characterization of the support.

As for the support, Figure 1 (a) shows the N_2 isotherm and Figure 1 (b) shows the mesopore size distribution of the powder SiO_2 prepared by the sol-gel methodology

with PEG-10K. As it can be observed, the sample displays a I+IV type isotherm typical for materials with both micro- and mesoporosity and the hysteresis cycle corresponds to the type H2 characteristic of bottle-necked pores or irregular interconnected porous structures with a wide mesoporous size distribution [25]. It must be noted that these two types of pores coexist with the macropores generated in the monolithic structure resulting from the decomposition of the PEG surfactant, giving rise to a hierarchical porous material. The BET surface area of the sample is $\sim 110 \text{ m}^2/\text{g}$.

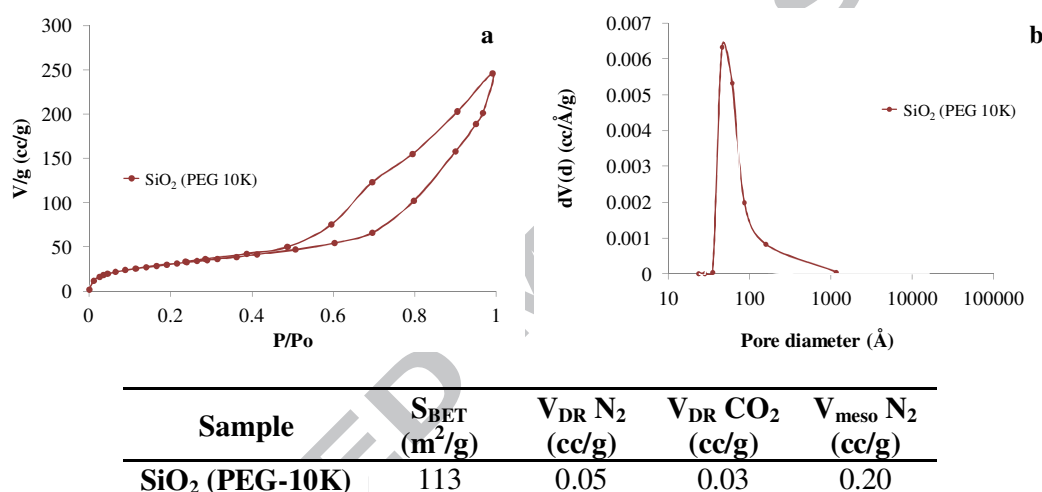


Fig. 1. (a) N_2 adsorption isotherm of the SiO_2 support prepared with PEG-10K and (b) BJH mesopore size distribution and porous texture characterization of the SiO_2 structure.

3.3. Characterization of the powder catalyst and the capillary microreactors.

A Pd/SiO_2 powder catalyst (1 wt% Pd) was prepared with the same surfactant (PEG-10K) as the one used in the SiO_2 monolith synthesis. ICP analysis indicated that it contains a metal amount close to the nominal metal loading (0.89 wt% Pd). TEM

analyses indicated that the average Pd particle size in the powder is slightly larger ($d=3.4 \pm 0.7$ nm) than the one obtained for the nanoparticles in the colloid, as observed in our previous report [7]. This effect has been already observed for similarly prepared catalysts and might be due to some metal sintering taking place during the impregnation process and also to a change in the shape of the nanoparticles due to deposition on the supports, as it has been previously stated [7].

Table 1 contains the characterization results of the Pd/SiO₂ and Pt/SiO₂ capillary microreactors prepared in this work.

Table 1. Characterization results of the prepared Pd/SiO₂ and Pt/SiO₂ microreactors.

Sample	Metal	d_{TEM} (nm)	D_{TEM} (%)	Amount of SiO ₂ (mg) ^a	Metal loading ICP (%)
MR-Pd	Pd	3.4±0.7	26.5	1.0	1.32
MR-Pt	Pt	3.5±0.7	26.0	1.0	1.20

^a Contained in each microreactor, estimated from the precursor concentration in the solution and the capillary length (20 cm).

For all the microreactors studied, the final metal loading determined by means of ICP-OES is very close to the nominal metal loading. Figure 2 shows the TEM micrographs of the catalysts within the microreactors, where it can be observed that the average metal particle size in the microreactors is similar to that obtained for the powder catalyst and no agglomerates of particles were detected in any case for the different samples.

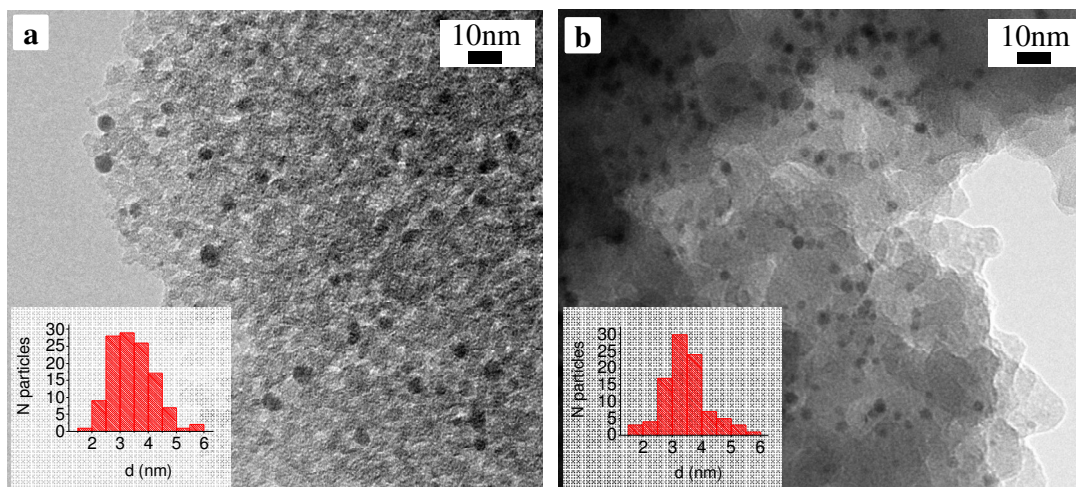


Fig. 2. TEM images of the microreactors (a) MR-Pd and (b) MR-Pt and the corresponding histograms showing the particle size distribution in each case.

Figure 3 shows, as a representative example, an optical microscopy of a SiO₂ monolith section from sample MR-Pd, as prepared and loaded with Pd nanoparticles. Figure 3 (a) shows the two SiO₂ monoliths inside the fused silica capillaries, where a continuous SiO₂ structure can be observed along the capillaries. The analysis of several sections of the samples indicated that the SiO₂ structures generated grow as continuous structures in all cases. Figure 3 (b) shows a magnification of the SiO₂ structures generated inside the capillaries. Due to impregnation with the metal, the sample changes its colour from white (pure SiO₂) to dark grey, corresponding to the metal-impregnated sample. From this analysis we observe that the monoliths prepared by this procedure are highly mechanically stable, since they retain their structure even after taking a small piece of monolith out of the capillary for its characterization. Furthermore, the capillaries could be handled without detachment of the monolith from the capillary walls.

Elemental mapping analyses (SEM-EDX) performed on several sections of these samples (Figures 3c - 3f) indicated that there is a very homogeneous distribution of the

metal nanoparticles throughout the SiO₂ structures. Spherical SiO₂ particles can be seen forming a continuous structure with a high degree of connected porosity, with the particles having an average size of 1-2 μm in the SiO₂ (see Figure S2). Since the macropores size is directly related to the skeleton particle size, a highly macroporous structure is therefore established. In addition, these materials are also highly mesoporous in character, according to the N₂ adsorption measurements (Figure 1). The continuous SiO₂ structure generated displays a surface enhancement factor F (defined as the surface area of the SiO₂ monolith (m²) with respect to the geometrical area of the empty capillary (m²)) of ~720 m²/m².

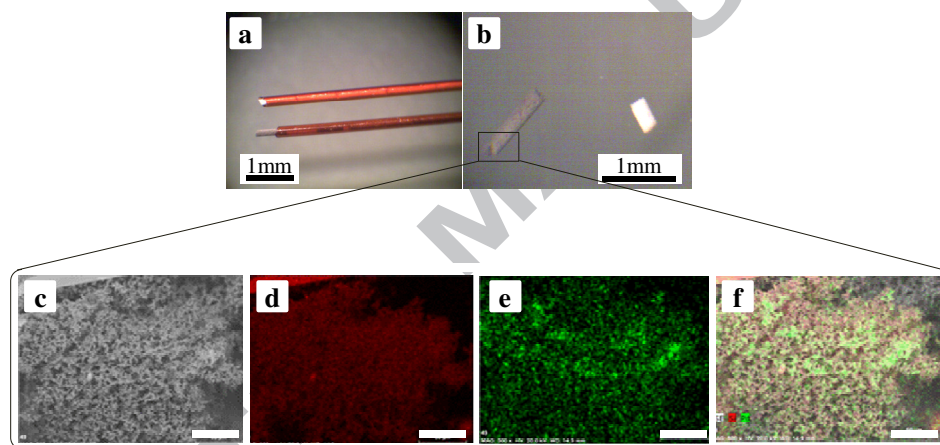


Fig. 3. Optical microscopy of the MR-Pd microreactor. (a) SiO₂ monoliths inside the fused silica capillaries and (b) magnification of the SiO₂ structures generated inside the capillaries. The white monolith is the as synthesized sample and the dark monolith is the Pd-loaded sample. Elemental mapping analysis (SEM-EDX) of the MR-Pd microreactor. The scale bar is 50 μm in all cases. c) SEM image of the section of the monolith analyzed. d) Si. e) Pd. f) Overlapping of Si (in red) and Pd (in green) elements detected in the sample.

3.4. Catalytic performance.

Figure 4 shows the comparison of the catalytic activity of the Pd/SiO₂ active phase in the microreactor (MR-Pd) and as powder (100 mg) under the same gas space velocity conditions.

As it can be observed, significant differences can be found between the two configurations. On the one hand, both active phases display a similar onset temperature for the reaction, which is ~130°C, and this is due to the similar nature of both catalysts. However, important differences in the CO conversion and selectivity can also be observed, achieving these two parameters higher values for the Pd/SiO₂ catalyst incorporated in the microchannel. In this sense, the Pd active phase in the microreactor displays 70% CO conversion at 180°C, whereas the powder Pd/SiO₂ catalyst barely reaches 20% CO conversion at the highest temperatures of the reaction. For the activity curve of the Pd microreactor (MR-Pd), the result seems to indicate that there is a tendency for the CO conversion to slightly decrease at high temperatures (above 170°C), which could be due, as previously observed for similar active phases [7] to the water-gas shift reactor becoming more relevant at high temperatures, as previously stated in the literature [27].

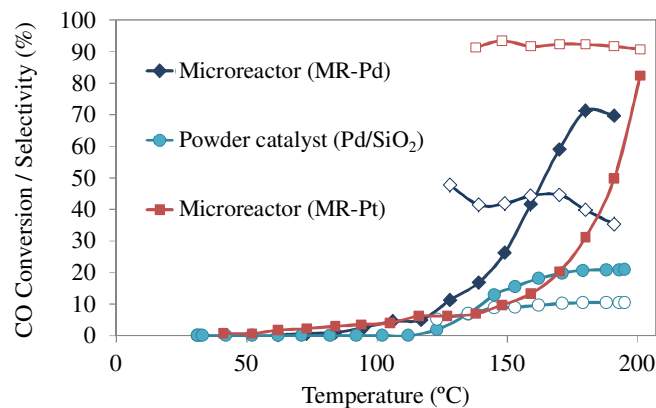


Fig. 4. Catalytic performance of MR-Pd (◆), MR-Pt (■) and Pd/SiO₂ powder catalyst (●). CO conversion (solid symbols, ●) and selectivity (hollow symbols, ○). Gas composition: 2% CO, 2% O₂, 30% H₂, balance He. GHSV=60000 ml g⁻¹ h⁻¹.

The enhanced performance of the microreactor with respect to the powder catalyst has been previously stated in the literature for several catalytic systems in microreactor configurations [11],[28],[29],[30]. In general, this enhanced microreactor behaviour is ascribed to mass and heat transfer processes favoured in the microchannels [4],[31],[27]. Also, since the catalyst is distributed as a highly interconnected porous structure inside the microchannel, this results in a favoured gas-catalyst interaction and provides a better catalytic performance of the metal nanoparticles, which is in accordance to the surface enhancement factor. Thus, the results found for the catalysts in the different reactor configurations in this work are in good agreement with those presented in the literature.

As observed in Figure 4, the powder Pd-based catalyst is also highly active in the undesired H₂ oxidation reaction and very low selectivity values have been obtained in the temperature interval analysed for this catalyst, reaching only ~10% throughout the reaction. However, the specific characteristics of the microreactors and the processes

that take place inside them reflect in an improved selectivity of the Pd/SiO₂ catalyst, obtaining selectivity values in the microchannels above those displayed by the powder catalyst, with values close to 50% over a wide temperature interval.

If we analyze these results in terms of activity of the surface metal atoms in the sample, we find that the Pd/SiO₂ catalyst in the microreactor exhibits a TOF value that is ~5 times larger (0.1 s⁻¹) than the one obtained for the powder catalyst (0.02 s⁻¹) at the same temperature (130°C) for low CO conversions. This further evidences the benefits of incorporating the catalyst within the microchannels for an enhanced performance of the active phase in this particular application.

In order to check the effect of residence time over the performance of the Pd/SiO₂ active phase, several experiments were performed at different gas space velocities for MR-Pd. These results (Figure S3) served to establish that the CO conversion diminishes from 100% to ~6% at the highest flow rates tested (450000 ml h⁻¹ g⁻¹). However, selectivity increases as the gas space velocity is increased (i.e. CO oxidation is favoured at higher space velocities). From these measurements, the results seem to confirm the idea that residence time has an influence over the performance of the catalysts designed for this particular application.

When compared to the MR-Pd microreactor, we can see that the Pt-based microreactor shows a significantly different activity, since the CO conversion curve is shifted towards higher temperatures. In this sense, T₅₀, defined as the temperature corresponding to 50% CO conversion for each sample, is 30°C higher for the Pt-based sample, compared to sample MR-Pd. Although this might mean a slightly lower activity for the Pt active phase, it can be seen that for the same amount of catalyst within the microchannels, the maximum CO conversion values achieved are slightly higher for Pt, with values above 80% at 200°C, compared to the ~70% obtained for the Pd active

phase. In addition, that active phase displays a much higher selectivity (under the same conditions) than the one based on Pd. At T_{50} , the selectivity of the Pt catalysts is twice as high as that of the Pd active phase. Also, for MR-Pt, the selectivity stays over 90% in the temperature interval analyzed, which is well within the operational window of the catalysts designed for this reaction. This result highlights the fact that Pt is a much more suitable option for this application, as previously noticed by other authors, with highly suitable parameters for the catalysts designed for the PrOx CO process.

The long term stability of the microreactors prepared for this reaction was also evaluated at different temperatures. For the Pd microreactor in the PrOx reaction, low temperature (140°C) was selected to analyze the performance of this active phase under the best conditions previously obtained (see Figure S3). For the Pt microreactor, 200°C was chosen as test temperature because of the good performance of the Pt catalyst at this temperature (see Figure 4).

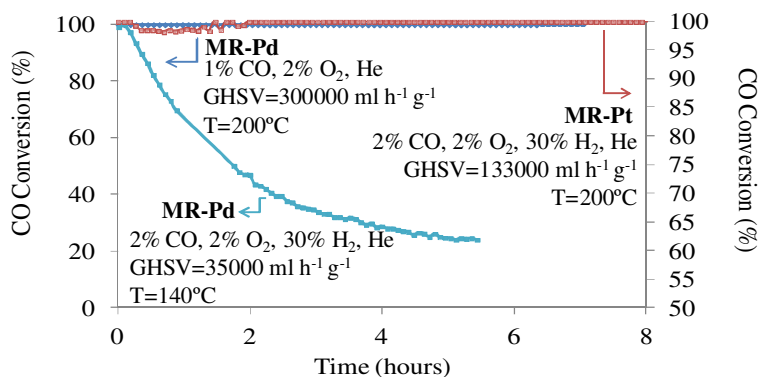


Fig. 5. Time-on-stream CO oxidation activity of MR-Pd and MR-Pt in the presence and absence of H_2 .

The results indicate that the catalytic activity remains constant at 100% CO conversion for a very short time and the Pd catalyst (MR-Pd) deactivates significantly for longer

application times (~75% after ~5 h of reaction). No sintering of the metal particles was detected by TEM in this case due to reaction conditions ($d=3.5 \pm 0.9$ nm). The reason for this deactivation could be related to H_2O being generated as a by-product inside the microreactor, since steam is known to affect the textural and/or structural properties of SiO_2 structure [32], but since this is only observed in the case of the Pd-based microreactor, this effect may be ruled out as the cause for this observation. In this respect, some alteration of the PVP structure or the stripping of the PVP by the action of steam could occur under the reaction conditions that would affect the Pd catalytic performance. An experiment of CO oxidation in the absence of H_2 (Figure 5) indicates that no loss of activity is detected for periods of time over ~7 h (in this case at $200^\circ C$) for MR-Pd, confirming the negative effect of steam over the Pd/ SiO_2 active phase. In the light of this significant deterioration of its catalytic activity when tested under realistic conditions, XPS analyses were performed on the Pd/ SiO_2 fresh and used microreactors (MR-Pd). The results indicated that the N/Pd ratio diminishes from 3.0 to 1.8 and that the Pd(0)/Pd(II) ratio also diminishes (from 4.3 to 2.6) when the reaction takes place. Since the only N source in the microreactors is the PVP surfactant, some degradation of its structure (or its removal from the Pd surface) may be inferred for the Pd-based samples. This could be due to the pressurization inside the capillary system during experiments, which is lower than 3 bars in all cases, but could cause (together with the presence of steam) the release of N-containing fragments from the structure of the polymer. Also, the loss of a significant amount of capping agent on the metal surface due to aging of the catalyst makes the nanoparticles more prone to oxidation under reaction conditions, as indicated by XPS and in good agreement with what was previously reported [8]. Considering that Pd selectivity is highly dependent on the PVP molecules anchored on the surface and that the deterioration of this protecting agent

strongly affects the selectivity of the catalyst, this deterioration of the Pd surface upon reaction justifies the impoverishment in selectivity with time for MR-Pd. Since no loss of catalytic performance has been observed for the MR-Pd sample in the absence of H₂ in the gas stream, no reasons to suspect alteration of the active phase in this case (relating to the Pd surface or the PVP on the nanoparticles) can be found.

As for the Pt microreactor, total CO oxidation can be obtained with the system displaying no loss of activity for several working hours (CO conversion ~100%) and with selectivity values ~50% throughout the experiment. These selectivity values differ significantly from those obtained in the non-isothermal experiment for this catalyst, indicating that the working regime is different in both cases. In this sense, the results shown in Figure 5 correspond to the steady-state performance of the catalysts, and therefore the thermodynamic selectivity values (as determined from equilibrium constants at those temperatures) is obtained (selectivity ~50%, for $\lambda=2$). On the contrary, for the results of MR-Pt shown in Figure 4, much higher selectivity values have been found (~90%), which are quite far from the values dictated by thermodynamics. Therefore, those values correspond to kinetic selectivity due to the non-isothermal experimental conditions.

From this result, significant differences between the Pd and the Pt systems can be observed. While both metal nanoparticles have been prepared and loaded on the SiO₂ support by the same experimental procedure, the Pd system shows a marked loss of selectivity when tested under isothermal conditions, whereas the Pt system maintains its activity over 8 h of continuous operation. These results point out that the Pd nanoparticles form an active phase which is more susceptible to modification during the reaction and is therefore not suitable for this particular application. In this sense, the critical effect of the electronic environment of Pd-based systems towards their catalytic

performance must be highlighted. On the other hand, the Pt system seems to be unaffected by the same reaction conditions and can withstand the working conditions for at least 8 h without deactivation or apparent modification of the electronic structure of the active phase, fulfilling the PrOx CO aimed catalysts requirements with very high selectivity towards the desired process.

When comparing the results obtained for the microreactors prepared in this work with other results found in the literature, Pt has long been reported as a more appropriate active phase for this reaction compared to other noble metal catalysts and is the most widely noble metal used in the latest works on catalysts for PrOx CO [33],[34],[35]. Pd has never been included in the catalyst compositions tested in microreactors, probably due to the poor performance in this application of traditionally synthesized Pd-based powder catalysts [36],[37]. The Pd-based microreactors prepared in this work present a good catalytic behaviour under a model gas composition to effectively purify H₂ streams for their further application. However, these microreactors strongly deactivate due to the instability of the active phase due to the degradation of the capping agent during the catalysis experiments. Regarding the deactivation of the catalysts in the long-term catalytic tests, it should be mentioned that only few works related to microreactors technology have addressed this issue [13],[31] and, in some cases, deactivation of the catalysts has also been found, even for Pt-based catalysts. This is not the case of the Pt/SiO₂ microreactor presented in this work that displays selectivity values at complete CO depletion of ~50%, very similar to that previously reported for other kind of microreactors in the literature [4],[12],[38]. It should be mentioned that in some cases where very good activity performances have been reported, selectivity results are not provided [27]. Also, in some cases, other catalyst compositions have displayed very

good performances in microreactors, but at temperatures well above those desirable for the PrOx reaction [39].

Microreactors designed for this reaction consist on thin films of the catalytically active phase deposited onto robust structures previously machined to prepare the microchannels. The microreactors described here present several positive aspects for this process, the main one being the outstanding catalytic performance displayed by such a small amount of catalyst, both in terms of activity and selectivity, and comparable to other microreactor configurations. In addition, these systems are small and highly flexible, without their manipulation affecting the nature of the sample inside them, which makes them highly suitable for small scale applications in which PrOx CO would be required, such as portable devices with on-board energy demand with micro fuel cells systems. For these reasons, the microreactor system presented here stands out as a promising purification device for systems which would need a relatively low flow (up to 7.5 ml/min) of high purity H₂ feed. Furthermore, scale up for larger applications (in situations where higher H₂ feeds are required) is a very simple process, since stacking of the capillaries in arrays where they are located in parallel would allow one to easily increase productivity in multichannel microreactors [40].

In addition to their outstanding performance in the PrOx CO reaction, these microreactors have also demonstrated a very good activity with high long term stability in the CO oxidation reaction both in absence of H₂ (for Pd-based microreactors) as well as for H₂-containing systems (for Pt-based microreactors), which also allows implementation of these materials in a different application.

4. Conclusions.

In summary, we have prepared Pd/SiO₂ and Pt/SiO₂ microreactors consisting on capillaries filled with a hierarchical monolith-based catalyst bed in order to obtain a homogeneous distribution of the active species along a microchannel by a simple and reproducible methodology. These microreactors behave more efficiently in terms of activity and selectivity than the reactor setup with the classical powder catalyst due to the superior mass and heat transfer processes that take place inside the microchannels. The possibility of achieving lower residence times in the microreactors is also responsible for the high selectivities obtained in these configurations.

These microreactors have proven to effectively purify a H₂ stream under the appropriate conditions. In this sense, Pt based microreactors achieve complete CO removal from the gas stream under time-on-stream experiments for more than 8 h without deactivation. Their very good catalytic behaviour, together with their flexibility, easily handling and ease of scale-up make these microreactors very good candidates for their application in the purification of H₂ streams for portable fuel cells or on-board applications.

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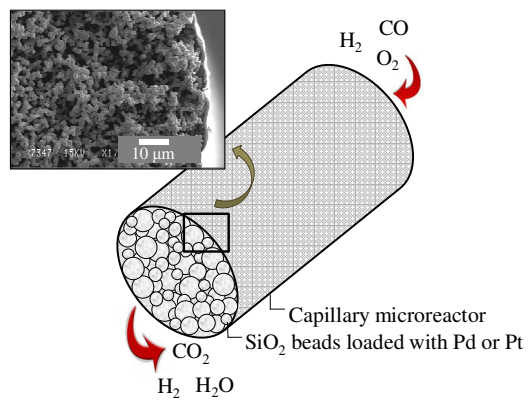
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Graphical abstract

Highlights

- Pd/SiO₂ and Pt/SiO₂ capillary microreactors were designed for the Preferential Oxidation of CO.
- Enhanced mass and heat transfer properties and catalytic activity in the microreactors.
- Residence time influences selectivity in the microreactors.
- Outstanding performance of the microreactors in the CO oxidation in the presence and absence of H₂.

ACCEPTED MANUSCRIPT