

Insights on palladium decorated nitrogen-doped carbon xerogels for the hydrogen production from formic acid

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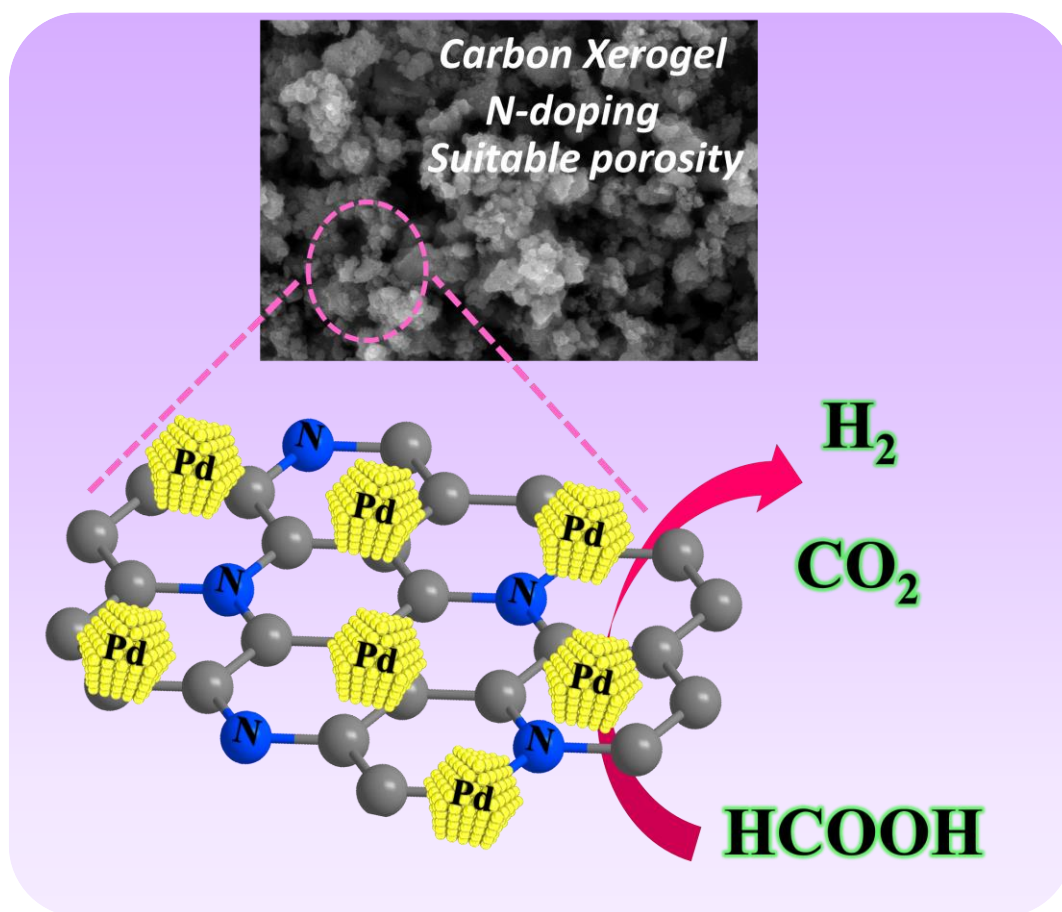
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Abstract

N-doped carbon xerogels synthesized from melamine-resorcinol-formaldehyde aqueous gels were used as supports for the preparation of Pd-based catalysts for the formic acid dehydrogenation reaction. The effect of the pore texture and nitrogen content of the carbon xerogels on the catalytic activity for the hydrogen production was investigated. It was observed that an appropriate nitrogen doping in a well-defined micro-mesoporous carbon xerogel enables the preparation of Pd catalysts with appreciable catalytic enhancement towards the formic acid dehydrogenation as compared to the N-free counterpart, reaching an initial TOF value of 2014 h^{-1} .

Keywords : Hydrogen production, formic acid, palladium nanoparticles, carbon xerogels, nitrogen doping.

Graphical Abstract



1. Introduction

The strengths of carbon materials as catalyst supports have been pointed out throughout the development of the heterogeneous catalysis, which is due to their attractive features, such as surface resistance to both basic and acid media, thermal stability, variable pore texture, controllable polarity and hydrophilicity by modifying their chemical surface properties, excellent electrical conductivity as well as cost-effective production and so forth [1,2]. Activated carbons have long been the most widely used supports of metal nanoparticles (NPs) rather than other carbon materials, but they show some shortcomings that should be circumvented in order to optimize the final catalytic systems for a given application. These drawbacks are in particular related to their pore texture. On the one hand, the mainly microporous nature (pores <2 nm) of activated carbons might limit the mass transfer of the molecules involved in a given reaction; on the other hand, as the loaded NPs are usually larger than 2 nm, they can be dispersed on the carbon external surface only, which will favor their aggregation and easy leaching, ultimately restricting the complete utilization of the loaded metal. In addition, the nano-architecture and nano-dimensions of activated carbons are not straightforwardly tunable for a particular catalytic application [3]. In this context, carbon gels (such as aerogels, cryogels and xerogels) are of great interest because their pore texture can be tuned at nanometer scale [4,5].

Besides this aspect, low amounts of functional groups also limit their practical application in catalysis, as NPs sintering and leaching may occur easily [6]. As a result, surface modification by functionalization and doping with heteroatoms (*e.g.* N, B, P or S) is widely used to palliate this issue. Among them, N doping is the most investigated case because the resulting materials display fascinating performances in numerous applications of industrial interest, such as Fischer–Tropsch synthesis and hydrogen generation, among other [7,8]. Nevertheless, even though N-doped carbon

materials have been extensively investigated, their application in catalytic reactions has been less reported since the main focus was put on energy conversion and storage [7,9]. This tendency has however changed over the last decade, since it has been recognized that N-groups can serve as anchoring sites for NPs, as well as modify their electronic features [10,11], thereby increasing the interest for the use of such structures in heterogeneous catalysis.

In particular, the use of N-doped carbon xerogels (N-CXs) has been satisfactorily explored for several applications, such as lithium batteries [12], oxygen reduction reaction [13,14], adsorption of heavy metal ions [15] and so on. In this study, we investigate the behavior of N-CXs as supports of Pd NPs designed to catalyze the formic acid (FA) conversion to hydrogen and carbon dioxide. This reaction has focused great efforts in the last decade, as FA is considered as a safe and promising candidate for hydrogen storage due to its low-toxicity, stability at room temperature, as well as easy transportation and handling. One of its most remarkable features is its high volumetric capacity of 53 g H₂ L⁻¹, which meets the latest requirements of the U. S. Department of Energy (DOE) for the onboard hydrogen storage in light duty fuel cell vehicles (40 g L⁻¹) [16]. An increasing number of publications dealing with the optimization of heterogeneous catalysts able to boost the FA dehydrogenation can be found in the literature. Efforts are made in particular to prepare structures that can compete with the generally more efficient homogeneous systems [17]. This vast literature includes studies where both the active phase and support features are modulated to achieve high-performance heterogeneous catalysts. Some of the approaches already considered by our research group encompass the addition of basic functional groups [18–20], the investigation of the effect of the Pd NPs size [21], the influence of PVP as capping agent of Pd NPs on the final catalytic performance [22], the preparation of alloyed NPs [18,23–25], or the impact of the support features [26,27].

Among the newly burgeoning alternatives considered in the optimization of the catalytic performance in the FA dehydrogenation, the use of N-doped carbon materials should be highlighted, as promising results regarding the impact of nitrogen functionalities on the Pd electronic features [11,28] or the stabilization of Pd NPs [29] have been reported. Herein we investigate the impact of two crucial parameters: the pore texture of the carbon support and the effect of nitrogen doping on the final catalytic performance of Pd-supported N-CX. The open pore texture of carbon xerogels constitutes an ideal scaffold for the synthesis of small and well distributed Pd NPs within the carbon porosity which, combined with nitrogen functionalities, results in high performance catalytic systems for the hydrogen production.

2. Experimental

2.1. Synthesis of melamine-resorcinol-formaldehyde carbon xerogels

N-CXs were synthesized from the polycondensation of resorcinol (R), formaldehyde (F) and melamine (M) as starting materials following a sol-gel protocol recently published [30]. The N-free CX was also prepared for comparative purposes. The polycondensation was performed in aqueous solution in presence of Na_2CO_3 (C), which is added to modify the initial pH value of precursors' solution.

The R'/F molar and dilution ratios were fixed with regard to previous work published by Job *et al.* [31]. The R'/F molar ratio was chosen equal to 0.5, where R' is the sum of resorcinol and melamine amounts. The dilution ratio D, *i.e.* the solvent to reactant molar ratio, was set at 5.7. While keeping R'/F and D constant, the R/M molar ratio was modified to obtain different levels of nitrogen doping; the R'/C molar ratio was also changed to obtain carbons with various pore textures. It should be mentioned that carbon gels, doped or not with N, are made of more or less spherical nodules that delimit mesopores or macropores (between them) and contain micropores

(within the nodules). The presence of either meso or macropores in the material depends on the size of the nodules, which varies with the composition of the precursors' solution.

In a typical synthesis, resorcinol and Na_2CO_3 were solubilized in deionized water at room temperature under magnetic stirring. Then, this solution was placed in a sealable flask under stirring together with formaldehyde. Since melamine is not soluble at the chosen concentration value at room temperature, the resulting mixture was heated in an oil bath up to 70 °C under magnetic stirring until a yellowish solution was obtained. Subsequently, the gelation process was performed at 85 °C for 72 h in an oven. Then, the gels were dried by vacuum evaporation at 60 °C for 24 h, by reducing the pressure progressively from 1.01×10^5 to 1.50×10^3 Pa. Finally, the gels were dried at 150 °C keeping the low pressure constant for 24 h.

The R/M and R'/C molar ratios, nitrogen amount determined by elemental analysis (EA) and names assigned to the supports are listed in Table 1. It is important to mention that all CXs presented micropores combined with mesopores or macropores depending on the R'/C and R/M molar ratios. All samples were denoted as *a*N-CX-*b*, being “*a*” the nitrogen content and “*b*” indicating the presence of either mesopores or macropores in each sample. For the same R'/C ratio (150), CXs with different pore textures and different nitrogen contents can be obtained (4N-CX-meso and 8N-CX-macro) by modification of the R/M ratio; supports with identical doping level were prepared by keeping constant the R/M ratio while modifying the R'/C ratio.

Table 1. Experimental conditions used for the different supports.

Sample	R/M	R'/C	N _{EA} (wt.%)
CX-meso	- ^a	800	- ^a
2N-CX-meso	7	150	2.1
4N-CX-meso	3	150	4.3
4N-CX-macro	3	250	4.2
8N-CX-macro	1	150	7.8

^{-a}: not relevant since no melamine was added.

2.2. Preparation of Pd/N-CX catalysts

Pd-supported catalysts were prepared by a conventional wet impregnation method. For that purpose, 0.4 g of CX support was dispersed in 20 mL of acetone and a solution of Pd(OAc)₂ (0.01M) was added so as to reach a final Pd loading of 0.5 wt.% [29]. The suspension was stirred for 4 h at room temperature and the solvent was subsequently evaporated under vacuum conditions at 55 °C using a rotary evaporator. After that, the Pd precursor was reduced with a H₂ flow (15 mL min⁻¹) at 300 °C for 2 h. The as-synthesized catalysts were denoted as Pd/*a*N-CX-*b*, according to the nomenclature previously described for the support counterparts.

2.3. Characterization

The pore texture of the CXs was characterized by means of physical adsorption-desorption of N₂ at -196 °C, using an automatic adsorption system (Micromeritics ASAP 2420 analyzer). All supports were outgassed overnight at 270 °C under 133 Pa. The specific surface area (*S*_{BET}) was calculated from N₂ adsorption data by applying the BET model in the relative pressure range from 0.01 to 0.1. The micropore volume (*V*_{DR}) was determined by using the Dubinin-Radushkevich equation to the adsorption branch of the isotherm up to *P*/*P*₀ = 0.1. The total pore volume (*V*_V) was calculated from the adsorbed volume at saturation (*V*_P) for samples whose isotherm reached a plateau at saturation, while mercury porosimetry was used otherwise. Mercury porosimetry measurements were performed using ThermoScientific Pascal 140 and 240 porosimeters. This analysis provides the pore volume corresponding to pores larger than 7.5 nm (*V*_{Hg}), *i.e.* the recorded mercury intrusion volume at 200 MPa. The pore volume vs. pore size (Figure S1) can be

plotted by calculating the pore size corresponding to each pressure value via Washburn's equation (Equation 1):

$$d_p(nm) = -\frac{4\gamma\cos\theta}{P(MPa)} \quad (\text{Eq. 1})$$

where γ is the mercury surface tension (0.48 N m^{-1}), θ corresponds to the contact angle of mercury on the solid (average value $\sim 140^\circ$) and P is the pressure at which the mercury intrusion occurs [32]. Notice that Equation 1 was used for macroporous CXs, while the BJH method was used for mesoporous samples by using the adsorption branch of the N_2 isotherm.

In the case of macroporous CXs, the combination of physical adsorption-desorption of N_2 and mercury porosimetry techniques was necessary to obtain an accurate value of the total pore volume (V_V) [30]. In this case, Equation 2 was used (assuming that the volume corresponding to pores of size ranging from 2 to 7.5 nm is negligible, which is indeed the case for micro-macroporous carbon gels).

$$V_V = V_{DR} + V_{Hg} \quad (\text{Eq. 2})$$

Scanning Electron Microscopy (SEM) analysis was performed to check the morphology and the sizes of the nodules present in the samples by using a JEOL JSM 840 microscope.

Concerning the characterization of the Pd catalysts, Transmission Electron Microscopy (TEM) was used to check the Pd NPs morphology by using a Hitachi H-800 electron microscope equipped with an energy-dispersive X-ray (EDX) detector operated at 200 kV. The average NP size was determined by measuring at least 100 particles from several micrographs with ImageJ software. X-ray photoelectron spectroscopy (XPS) data were collected using an ESCA 3400 Electron Spectrometer. Pd K-edge XAFS spectra were recorded using a fluorescence-yield collection

technique at the beamline 01B1 station with an attached Si (111) monochromator at SPring-8, JASRI, Harima, Japan (2017B1081 and 2017B1084). The EXAFS data were treated using the Rigaku EXAFS analysis software.

2.4. Catalytic tests

The catalytic activity of the as-synthesized samples in the dehydrogenation of FA was evaluated by using a burette system. To this end, the catalyst was placed into a reaction vessel with a reflux condenser and equipped with a gas burette. The vessel was purged with inert gas, and then an aqueous solution containing HCOOH and HCOONa (HCOOH/HCOONa = 9/1; 1 M; 10 mL) was added to the reaction vessel. The gas generated (H₂ + CO₂) at 75 °C was monitored and TOF values (h⁻¹) were calculated using the following equation:

$$TOF (h^{-1}) = \frac{P_{atm} V_{H_2}}{R T t N_{Pd}} \quad (Eq. 3)$$

where P_{atm} is the atmospheric pressure, V_{H_2} is the produced volume of H₂, R is the perfect gas constant, T is the reaction temperature (75 °C), N_{Pd} is the Pd amount (mol), and t is the reaction time.

3. Results and discussion

3.1. Characterization of the support

As mentioned above, several CXs with different pore textures and nitrogen contents were synthesized by modifying the initial composition of the precursor solution. Figure 1 shows the N₂ adsorption-desorption isotherms of these CXs used as catalyst supports; numerical values associated to these isotherms are presented in Table 2. It can be observed that all supports present a gas uptake at low relative pressures, indicating the presence of a significant volume of micropores. The N-free support (CX-meso) displays the highest adsorption volume at low relative

pressure while the adsorbed volume for all N-CXs was smaller in this region, indicating a decrease in S_{BET} compared to CX-meso support (307 to 590 m^2/g instead of 726 $\text{m}^2 \text{g}^{-1}$) and, in parallel, a lower micropore volume V_{DR} (0.13 to 0.25 instead of 0.29 cm^3/g).

Regarding the high relative pressure region, two N-CXs (2N-CX-meso and 4N-CX-meso) as well as the non-doped CX support (CX-meso) present a hysteresis loop associated to the presence of mesopores. Taking into account that these supports have a significant micropore volume, it can be concluded that these samples display a combination of Type I and IV isotherms, according to IUPAC classification. The hysteresis loop of both CX-meso and 4N-CX-meso occur at the same pressure, indicating that both supports have a similar average pore size (16 and 14 nm, respectively), which is calculated from the BJH method (Table 2). However, the hysteresis loop of the 2N-CX-meso support is located at lower relative pressures, indicating a decrease in the average pore size. No hysteresis loop is observed for 4N-CX-macro and 8N-CX-macro samples. Furthermore, reaching the saturation pressure in the high relative pressure region was difficult in the case of these two samples, indicating the presence of macropores that cannot be properly characterized by N_2 adsorption-desorption isotherms. In this case, N_2 adsorption-desorption analysis was combined with mercury intrusion porosimetry measurements to obtain an accurate value of the total pore volume.

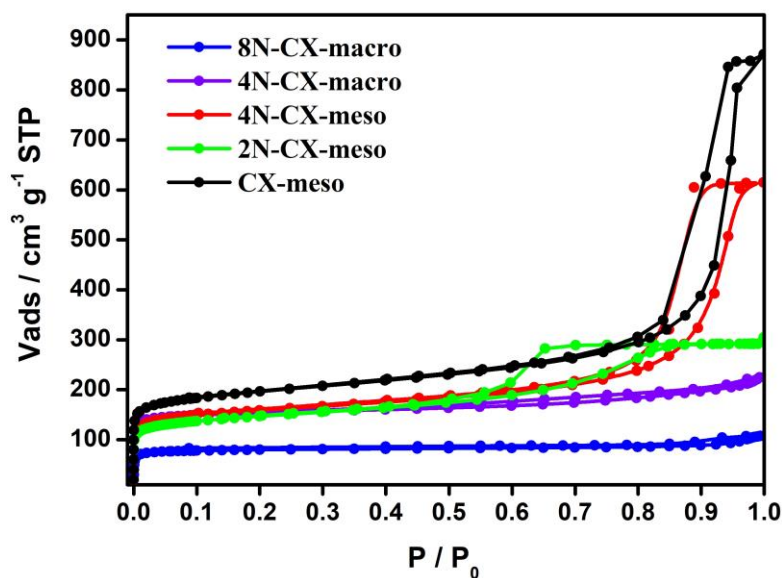


Figure 1. N₂ adsorption–desorption isotherms at – 196 °C for all supports.

The average pore size of 4N-CX-macro was estimated from the starting point of mercury intrusion (see Figure S1) using Washburn’s equation (Eq. 1). In the case of 8N-CX-macro, mercury intrusion does not occur (see Figure S1): the sample underwent crushing during the pressure increase and the average pore size could not be calculated because the Washburn’s equation is not applicable. One can however state that the sample contains macropores, since the volume crushing upon pressurization corresponds to 0.42 cm³/g (Table 2).

Table 2. Porous texture properties for N-CXs.

Sample	S _{BET} / m ² g ⁻¹	V _{DR} / cm ³ g ⁻¹	V _{Hg} / cm ³ g ⁻¹	V _V / cm ³ g ⁻¹	Pore size / nm
CX-meso	726	0.29	-	^a 1.46	^c 16
2N-CX-meso	545	0.22	-	^a 0.46	^c 6
4N-CX-meso	590	0.24	-	^a 0.94	^c 14
4N-CX-macro	587	0.24	1.36	^b 1.60	^d 1180
8N-CX-macro	307	0.13	0.42	^b 0.65	^e

^aV_V = V_P (obtained from the plateau of the isotherms), ^bV_V = V_{DR} + V_{Hg}, ^ccalculated by the BJH method, ^dpore size = dp, calculated by Washburn’s equation, ^enot calculable (crushing).

The morphology of CXs with micro-mesoporous and micro-macroporous textures was analyzed by means of SEM and micrographs of two representative supports (4N-CX-meso and 4N-CX-macro) are shown in Figure 2. Both supports were synthesized with the same melamine amount and different R'/C ratio so as to obtain different pore textures. The 4N-CX-meso support (low R'/C ratio) displays smaller carbon nodules than 4N-CX-macro (high R'/C ratio), which can be directly associated to the average pore size [30]. Indeed, since the presence of meso- or macropores is related to the size of the voids between the nodules of the xerogels: large nodules lead to macropores in the structure, while small nodules produce mesopores.

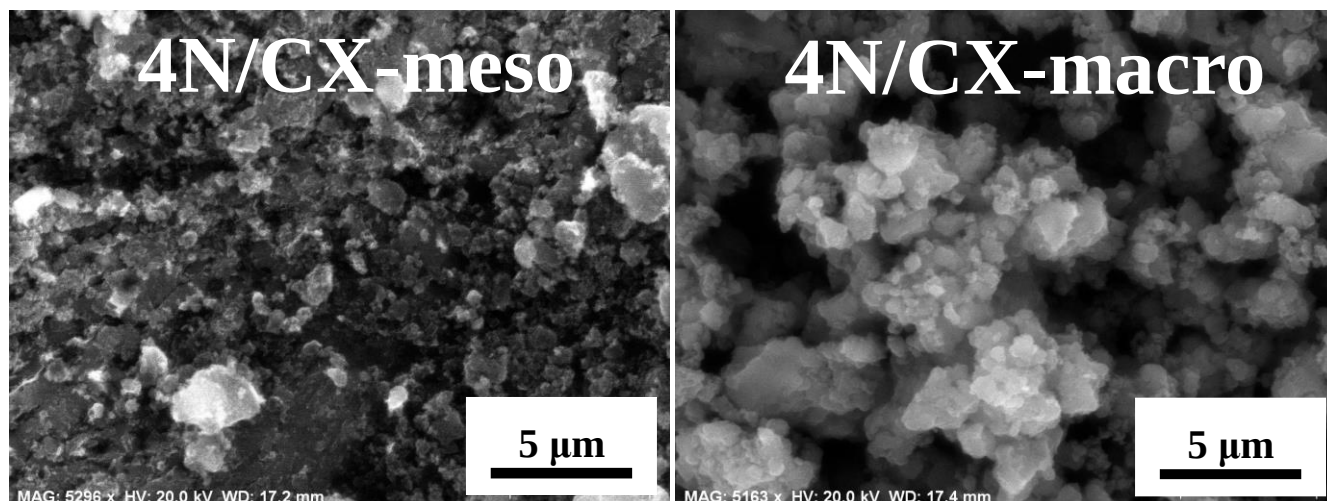


Figure 2. SEM micrographs of 4N/CX-meso and 4N/CX-macro.

3.2. Characterization of the catalysts

Figure 3 shows the TEM micrographs along with the pertinent histogram of NPs size distribution and average NP size for each sample. The average NP size ranges from 2.2 to 8.3 nm and, excluding sample with 8 wt.% of nitrogen (Pd/8N-CX-macro), the NPs display a spherical shape, very narrow size distribution and homogeneous dispersion on the CXs. The nitrogen-free sample (Pd/CX-meso) shows an average Pd NPs size of 3.4 nm, while samples with low and

moderate nitrogen doping display a smaller average size of 2.7 nm for 2 wt.% doping (Pd/2N-CX-meso) and 2.3 and 2.2 nm for 4 wt.% of doping (samples Pd/4N-CX-meso and Pd/4N-CX-macro, respectively). Furthermore, as can be seen from the histograms, a narrower NPs size distribution is observed for samples with 2 and 4 wt.% of nitrogen as compared to the nitrogen-free catalysts. According to these results, it seems that a low (2 wt.%) and moderate (4 wt.%) nitrogen doping on CXs might favour the synthesis of small Pd NPs by acting as basic coordination sites [33,34], while a further addition of nitrogen in the carbon support (up to 8 wt.%) might have a negative effect by giving rise to Pd aggregation. The variation of the NPs size with the nitrogen loading might be related to the interaction between Pd precursor and support surface. It might be expected that a weaker interaction leads to larger NPs due to aggregation during reduction under H₂ [35]. In this line, nitrogen atoms can interact with Pd²⁺, avoiding the aggregation of Pd during the reduction. However, the larger NPs observed for sample Pd/8N-CX-macro might indicate that the reduction of Pd precursor is hindered in the 8N-CX-macro support, which can be related to lowered reducibility of Pd precursor when a large content of Lewis basic sites are present on the support [35]. Furthermore, the large NPs observed in Pd/8N-CX-macro could be also partially due to the lower surface area that characterizes this CX.

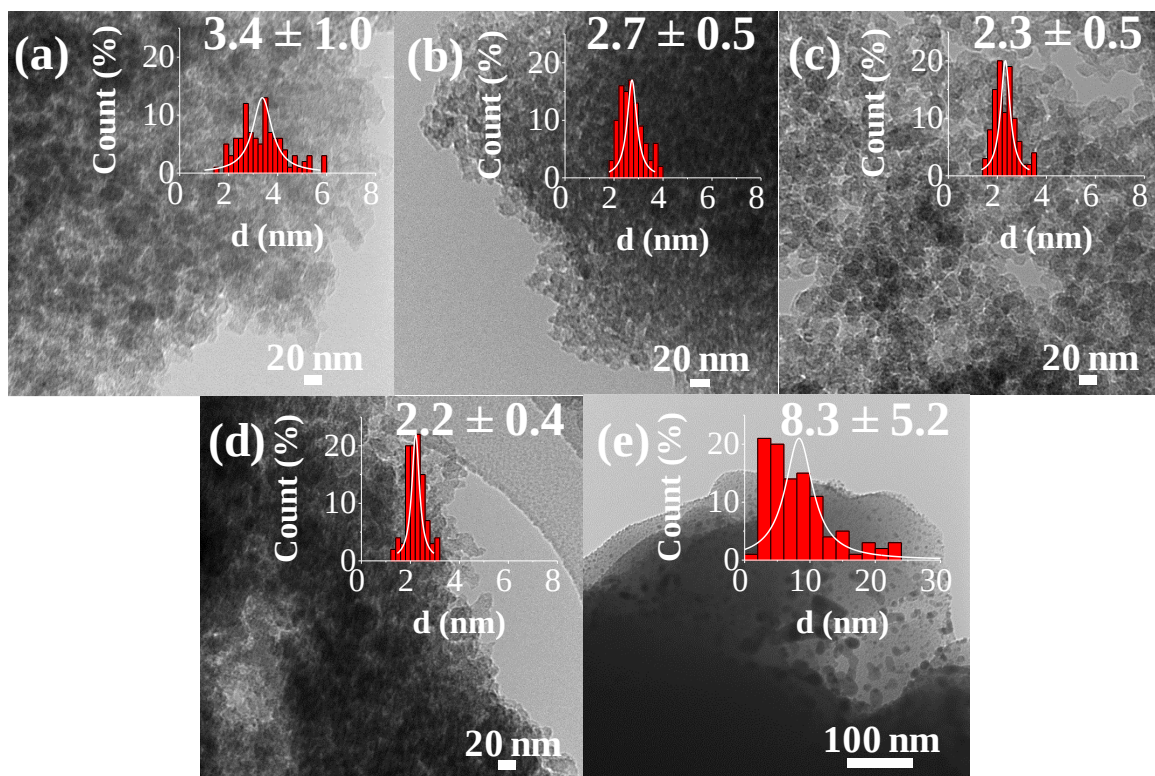


Figure 3. TEM micrographs of the five Pd/CX catalysts: (a) Pd/CX-meso; (b) Pd/2N-CX-meso; (c) Pd/4N-CX-meso; (d) Pd/4N-CX-macro; (e) Pd/8N-CX-macro

X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the electronic state of Pd and N. Regarding nitrogen functionalities, Figure 4 shows the deconvoluted N 1s XPS spectra of Pd/4N-CX-meso as a representative example, all other spectra being similar.

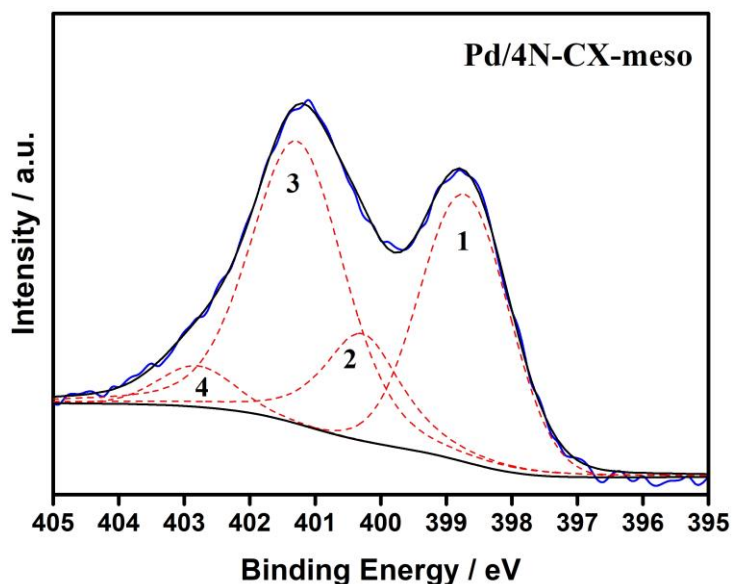


Figure 4. N 1s XPS spectra of Pd/4N-CX-meso.

Four different contributions can be distinguished at around 398.7, 400.2, 401.1 and 402.9 eV. The first and third binding energies are related to the presence of pyridinic and quaternary (graphitic) nitrogen groups in the carbon network, respectively [30,36]. Both nitrogen functionalities are the most important contributions to the total nitrogen amount, which is in agreement with nitrogen precursors carbonized at a temperature above 600 °C [7,37]. The second peak corresponds to pyrrolic/pyridone nitrogen groups, while the fourth peak, which is not very intense, is related to the presence of more oxidised forms [36,38,39]. Table 3 summarizes the XPS data of nitrogen speciation for all four N-containing catalysts. The important contribution of $N_{\text{pyridinic}}$ and $N_{\text{graphitic}}$ should be mentioned, as these functionalities increase the local basicity of the final material [40], which is expected to be a pivotal aspect in the final catalytic ability for the studied application.

Table 3. Relative content of nitrogen forms calculated from N 1s XPS spectra (at.%).

Sample	N _{pyridinic}	N _{pyrrolic/pyridone}	N _{graphitic}	N _{oxidized}
Pd/2N-CX-meso	36.1	10.8	46.8	5.2
Pd/4N-CX-meso	35.1	16.7	45.2	5.0
Pd/4N-CX-macro	34.5	13.6	44.0	5.4
Pd/8N-CX-macro	38.4	16.0	39.4	6.3

Pd 3d peaks of N-containing catalysts are shifted to higher binding energies compared to the N-free sample (See Figure S2 and Table S1), confirming the Pd-N interaction and the modification of the electronic properties of Pd. To get further insight into the electronic state of Pd, X-Ray absorption measurements were performed. Figure 5 shows the Fourier Transforms (FT) k^3 -weighted Pd K-edge extended X-ray absorption fine structure (EXAFS) for the catalysts with different nitrogen content along with Pd foil and PdO as reference samples. As for reference samples, Pd foil displayed a main peak centred at 2.5 Å corresponding to a Pd-Pd bond, while PdO shows two peaks centred at 1.6 and 3.0 Å, ascribed to Pd-O and Pd-Pd bonds, respectively. In the case of the N-free catalyst (Pd/CX-meso), the presence of the main peak at 2.5 Å confirmed the metallic state of Pd NPs, but the presence of PdO on the surface of the NPs cannot be ruled out. Interestingly, some differences were observed for the N-containing catalysts. Samples with low and moderate nitrogen content (Pd/2N-CX-meso and Pd/4N-CX-meso) showed two main peaks, centred at 1.5 and 2.5 Å, respectively, while sample Pd/8N-CX-macro displayed only one peak at 2.5 Å (Pd-Pd). As previously reported for electronically modified Pd catalysts supported on N-doped carbon, the first peak observed in Pd/2N-CX-meso and Pd/4N-CX-meso (1.5 Å) might be ascribed to the Pd-O(N) bond [11]. The inexistence of Pd-N peak in sample Pd/8N-CX-macro might be in agreement with the less important Pd-N interaction, which in turn can be related to the

fact that the Pd NPs are larger in this sample. Furthermore, since the specific surface area of 8N-CX-macro is lower compared to the other nitrogen-containing samples, the less important Pd-N interaction observed might be also related to less nitrogen functions accessible to the Pd NPs.

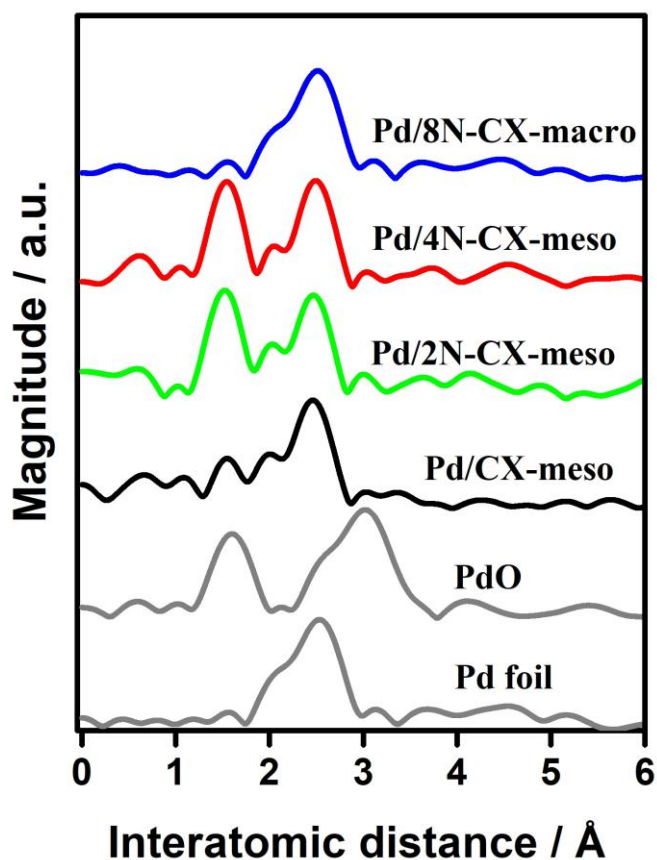


Figure 5. Pd K-edge FT-EXAFS spectra.

3.3. Catalytic activity

The time course for the hydrogen production from FA was monitored periodically as shown in Figure 6. No induction time was observed for any of the catalysts, but important differences were seen along the reaction course. Firstly, it should be noticed that the N-free sample (Pd/CX-meso) showed a poor catalytic ability for the FA dehydrogenation reaction, generating only 8 mL of gas

($\text{H}_2 + \text{CO}_2$) after 5 min, time after which the reaction ceased. Interestingly, the reaction was promoted by the N-containing samples, with the exception of Pd/8N-CX-macro, whose behaviour is very similar to that of the N-free sample. Among the N-containing samples, several effects should be mentioned. On the one hand, the pore texture of the support seems to play a key role in the catalytic ability. Indeed, the samples displaying a micro-mesoporous texture (Pd/2N-CX-meso and Pd/4N-CX-meso) display a better behavior than those characterized by a micro-macroporous texture. This effect is evidenced by the comparison of samples Pd/4N-CX-meso and Pd/4N-CX-macro, both bearing the same nitrogen content. In the first case, the gas evolution occurred gradually with the reaction time and reached a total generation of 100 mL, while the reaction was dramatically sluggish after 5 min for sample Pd/4N-CX-macro with a final gas production of 28 mL. It is expected that the carbon porosity impacts the accessibility of FA molecules to the catalytic sites. The pore size itself has no effect since the reaction occurs in liquid phase and the diffusion mechanisms is molecular diffusion, in which the liquid molecules see other liquid molecules, not the pore walls of the catalyst. It should be noticed that a different situation would be encountered in gas phase reactions, where Knudsen-type diffusion takes place [41]. However, an increase of carbon particle void fraction (micropores excluded, i.e. meso-macropore volume, $V_V - V_{\text{DR}}$) would lead to a decrease of diffusional limitations if mass transport between the nodules rules the system. Here, no direct relationship can be found between the meso-macropore volume and the catalytic performances, indicating that the pore texture of the support is not the sole responsible for the observed variations in catalytic activity. Note however that the granulometry of the carbon particles was not controlled and might also vary from one catalyst to another, which could also impact mass transport.

The nitrogen content is an additional aspect to be considered while optimizing the catalytic ability in the present application. According to the tendency observed in this study, the optimum nitrogen content among those investigated under the present experimental conditions was 4 wt.%. As observed from TEM analysis, further addition of nitrogen on the studied CX seems to favor the agglomeration of Pd, attaining Pd NPs with an average NPs size of 8.3 ± 5.2 nm and uneven distribution on the carbon support, ultimately declining the catalytic ability towards the FA dehydrogenation reaction. Nevertheless, the differences observed might not be merely ascribed to the effect of the nitrogen content in the NPs size, but also to its effect in the Lewis basicity of the material as well as in the Pd electronic properties, both related to the strength of the interaction with FA molecules and ultimately affecting the FA decomposition ability. It has been reported that electron deficient Pd interacts better with reaction intermediates such as formate ion, which is a key intermediate in the FA dehydrogenation reaction [42]. The shift of the binding energy towards higher values observed in the Pd 3d XPS spectra for the N-containing samples might indicate the existence of such electron deficient Pd species and could be one of the key aspects in attaining enhanced catalytic performance as compared to the N-free counterpart.

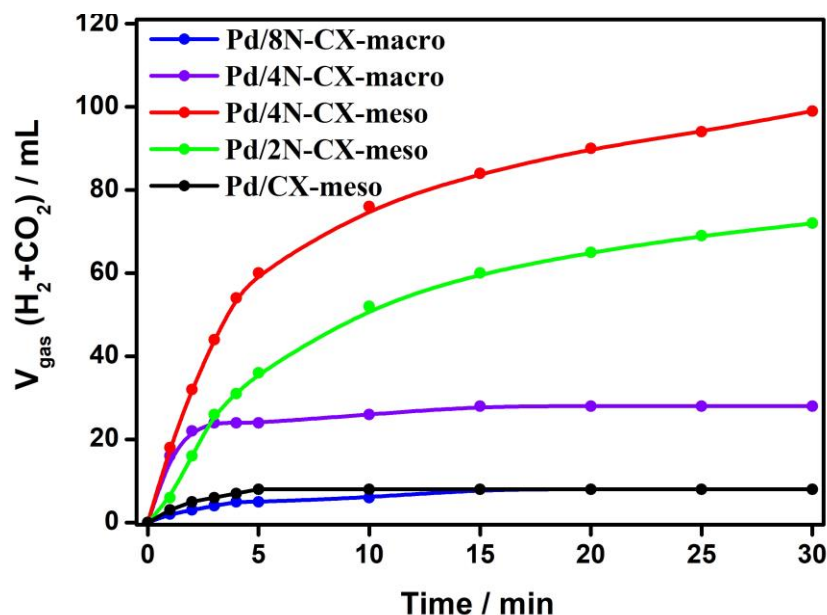


Figure 6. Time course of reaction in the H₂ production from formic acid at 75 °C.

The positive impact of N-functionalities on the performance of carbon-supported catalysts for the FA dehydrogenation reaction has also been recently reported by our research group [34] by performing both experimental and theoretical studies and concluding that the N-functional groups foster both the O-H cleavage as well as the H₂ desorption step. Similar conclusions were drawn using phenylamine-grafted PdAg/SBA-15 [19], as well as PdAg/basic resins [18]. Similarly, the effect of nitrogen doping was also addressed by Bulushev *et al.* in their studies on vapor-phase FA decomposition [29,43]. Remarkably, the best performing catalyst among those investigated in the present study reached an initial reaction rate of 540000 mL h⁻¹ g⁻¹ (Pd) with a turnover frequency (TOF) of 2014 h⁻¹ on the basis of the total Pd loading, which is higher than any value achieved by several reported Pd-based catalysts (see Table S2).

It should be noticed that, even though some studies reporting the importance of the nitrogen speciation (*i.e.* pyridinic-N) can be found in the recent literature [28], the effect of the nitrogen

content in the final catalytic performance has been hardly investigated. Herein we address for the first time the application of N-doped carbon xerogels with controlled porosity and nitrogen content for the FA dehydrogenation reaction and we expect that this study can pave the way towards the engineering of new doped carbon materials with tailored porosity and basic features for the hydrogen production from hydrogen carrier molecules.

4. Conclusions

In this work, Pd catalysts supported on nitrogen doped carbon xerogels were prepared and tested for the formic acid dehydrogenation reaction in liquid phase. The experimental conditions used in the synthesis of the supports were modulated so as to obtain carbon xerogels with different pore texture and nitrogen contents. The characterization of the resulting Pd catalysts indicated that an appropriate nitrogen doping, which in this case was 4 wt.%, plays a key role in affording highly dispersed and small Pd nanoparticles. The presence of nitrogen in the samples is responsible for the increase of Lewis basicity of the resulting materials as well as for the changes in the electronic features of the Pd species. All these aspects, together with the adequate pore texture developed in the carbon xerogels are vital elements in the preparation of suitable catalysts for the formic acid dehydrogenation reaction. The most active catalysts among those investigated in this study showed an initial TOF value of 2014 h^{-1} on the basis of the total Pd loading, which is a very promising result for a monometallic catalyst.

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