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# Hydrogen production from formic acid decomposition in the liquid phase using Pd nanoparticles supported on CNFs with different surface properties†

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The development of safe and efficient H<sub>2</sub> generation/storage materials toward a fuel-cell-based H<sub>2</sub> economy as a long-term solution has recently received much attention. Herein we report the development of preformed Pd nanoparticles supported on carbon nanofibers (CNFs) via sol-immobilisation and impregnation techniques as efficient catalysts for the liquid phase decomposition of formic acid to H<sub>2</sub>. We used CNFs as the preferred choice of support and treated at three different temperatures for the deposition of Pd nanoparticles. They were thoroughly characterised using XRD, XPS, SEM-EDX, TEM, Raman spectroscopy and BET. We observed that the Pd particle size, metal exposure and CNF graphitisation grade play an important role in catalytic performance. We found that Pd/CNFs prepared by the sol-immobilisation method displayed higher catalytic performance than those prepared by the impregnation method, due to the smaller Pd particles and high Pd exposure of the catalysts prepared by the first method. Moreover, we have shown that the best results have been obtained using CNFs with a high graphitisation degree (HHT). DFT studies have been performed to gain insights into the reactivity and decomposition of formic acid along two-reaction pathways on Pd(111), Pd(011) and Pd(001) surfaces.

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## Introduction

To meet the increasing energy demand without further damage to the environment, alternative energy sources have been considered. Amongst them, hydrogen is becoming one of the most promising energy sources for the future. Its versatility lies in the possibility to convert it to electricity or heat through electrochemical and catalytic processes.<sup>1</sup> However, due to technical obstacles for controlling both the storage and release of hydrogen, general utilisation is limited. Therefore, research

is being focused on exploring and finding storage materials that are able to fulfil these requirements.

The physical storage of hydrogen has been demonstrated within porous networks such as carbon materials,<sup>2</sup> metal-organic frameworks,<sup>3</sup> zeolites,<sup>4</sup> clathrate hydrates,<sup>5</sup> and organic polymers.<sup>6</sup> However, hydrogen can also be part of a compound *i.e.* it can be chemically stored, requiring a decomposition process to release it from compounds such as, ammonia borane,<sup>7</sup> amines,<sup>8</sup> sodium borohydride,<sup>9</sup> alcohols,<sup>10</sup> hydrous hydrazine<sup>11</sup> and formic acid.<sup>12</sup>

Formic acid is a safe and convenient liquid storage material capable of releasing hydrogen under mild conditions. It may be produced during biomass upgrading, such as the hydration of 5-HMF, as well as by direct hydrogenation of CO<sub>2</sub>. Several properties such as its high stability in the absence of catalysts, being a liquid under ambient conditions, its high volumetric hydrogen content (4.4 wt%), its environmentally benign nature and nontoxicity, have promoted its importance in the field, becoming one of the most studied and promising liquid hydrogen carriers according to the U.S. Department of Energy. The decomposition of formic acid can proceed following two pathways, namely dehydrogenation (HCOOH → CO<sub>2</sub> + H<sub>2</sub>, ΔG =

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−48.4 kJ mol<sup>−1</sup>) and dehydration (HCOOH → CO + H<sub>2</sub>O, Δ*G* = −28.5 kJ mol<sup>−1</sup>). Acidity or high temperature during the reaction usually promotes the dehydration pathway. Ultrapure hydrogen is necessary for the generation of energy with fuel cell devices, and since they are poisoned by CO, inlet CO concentration should remain below 20 ppm, otherwise a loss of long-term performance can occur. Mild conditions are also of key importance since these fuel cells are expected to supply energy to portable devices with a low heat management profile.

The homogeneous or heterogeneous catalytic decomposition of formic acid to hydrogen has thus been the topic of much investigation for the last ten years. However, issues such as the use of organic solvents, alongside separation problems, prevent the use of homogeneous catalysts in the device fabrication.<sup>13,14</sup> Accordingly, heterogeneous catalysts have received much attention in the past few years. In this context, Pd, Au or Ag and their alloys have been widely studied.<sup>3,13,15–26</sup> Numerous types of materials have been used as catalyst supports for formic acid dehydrogenation, *i.e.* activated carbon,<sup>23–25</sup> zeolites,<sup>26</sup> macroreticular resins,<sup>15</sup> amines<sup>16</sup> and MOFs.<sup>3,17,18</sup> Carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have also been successfully used as supports for the synthesis of supported metal nanoparticles for a wide range of important catalytic applications such as alcohol oxidation,<sup>27,28</sup> nitrite reduction,<sup>29</sup> oxygen reduction reactions,<sup>30,31</sup> and hydrogen generation.<sup>32,33</sup> When compared with other supports, CNFs present advantages such as the possibility to tailor the microstructures of CNFs by selecting growth techniques, the control of the surface chemistry by surface modification and the facile recovery of the metal by burning off the support.<sup>32</sup> Moreover, carbon nanofibers present high mechanical strength, high thermal and electrical conductivity and good chemical stability in aggressive media.<sup>34</sup> The carbon nanofibers used in this work are produced on a large scale and have applications in industry.<sup>35</sup>

In the present work, we report the effect of different types of CNFs as potential supports for depositing Pd nanoparticles and

the catalytic performance in the case of the liquid phase decomposition of formic acid under mild reaction conditions. The CNFs used are: (1) pyrolytically stripped (PS-CNF), (2) low-heat treated (LHT-CNF) and (3) high-heat treated (HHT-CNF). The choice of the described CNFs allowed us to study the effect of the degree of CNF graphitisation. Furthermore, we studied the effect of these CNFs on the supported Pd particles' morphology prepared by a sol immobilisation method (using polyvinyl alcohol (PVA) as a stabiliser and NaBH<sub>4</sub> as a reducing agent) and impregnation method – both commonly used preparative methodologies in academic and industrial groups. The characterisation of these catalysts was thoroughly performed by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX), temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD), Raman spectroscopy and BET (Brunauer–Emmett–Teller) surface area analysis. The catalyst performance study towards aqueous formic acid decomposition was carried out in a batch reactor. Finally, periodic density functional theory (DFT) calculations were employed to gain insights into the energy profiles along different decomposition pathways on Pd(001), Pd(011) and Pd(111) surfaces.

## Experimental

### Materials and chemicals

Formic acid (≥95%, Cat. W248703) and succinic acid (99%, Cat. S3674-100G) were obtained from Sigma Aldrich. Deionised water was used as the reaction solvent. CNFs PR24-PS, PR24-LHT and PR24-HHT were purchased from Applied Science Company. The CNFs consist of tubular fibres with an average diameter of 80 ± 30 nm and a specific surface area of around 50 m<sup>2</sup> g<sup>−1</sup>. Schlögl and co-workers previously performed thorough characterisation of these materials.<sup>35</sup> PS grade carbon nanofibers are produced by pyrolytically stripping the CNFs to remove polyaromatic hydrocarbons covering the outer CNF surface. LHT grade carbon nanofibers are produced by treating the CNFs at 1500 °C which carbonises any chemical vapour deposited carbon from the surface of the CNFs. HHT grade carbon nanofibers are produced by treating the CNFs at 3000 °C creating the most graphitic carbon nanofibers.

### Preparation of the Pd/CNF catalyst series

**Immobilisation method of Pd sol.** The following experimental protocol was used for the synthesis of Pd supported nanoparticles. Na<sub>2</sub>PdCl<sub>4</sub>·2H<sub>2</sub>O (Pd: 0.094 mmol) and freshly prepared PVA solution (1 wt%) were added (PVA/Pd (wt/wt) = 0.25) to 100 mL of H<sub>2</sub>O. After 3 minutes, a freshly prepared aqueous solution of NaBH<sub>4</sub> (0.1 M, NaBH<sub>4</sub>/Pd (mol mol<sup>−1</sup>) = 8) was added to the yellow-brown solution under vigorous magnetic stirring. A brown Pd<sup>0</sup> sol was immediately formed. The UV-visible spectrum of the palladium sol was recorded for ensuring the complete reduction of the Pd<sup>II</sup> precursor. Within a few minutes from its generation, the suspension was acidified at pH 2 using sulfuric acid, and the support (1 g) was added

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under vigorous stirring. After one hour, the catalyst was filtered and washed several times with distilled water (2 L) to remove species, such as Na<sup>+</sup> and Cl<sup>-</sup>, and to reach neutral pH. The samples were dried in an oven at 80 °C for two hours under static air. The amount of support added was calculated to obtain a final nominal metal loading of 1 wt%. The obtained catalysts were labelled Pd<sub>SI</sub>/CNF-HHT, Pd<sub>SI</sub>/CNF-LHT and Pd<sub>SI</sub>/CNF-PS.

**Impregnation followed by chemical reduction with sodium borohydride.** Na<sub>2</sub>PdCl<sub>4</sub>·2H<sub>2</sub>O (Pd: 0.094 mmol) diluted in 100 mL of H<sub>2</sub>O was added to the support (1 g) and stirred vigorously. After 6 hours, a freshly prepared aqueous solution of NaBH<sub>4</sub> (0.1 M, NaBH<sub>4</sub>/Pd (mol mol<sup>-1</sup>) = 8) was added and stirred for six more hours. After one hour, the catalyst was filtered and washed several times to ensure the removal of the material arising from the reduction treatment. The samples were dried at 80 °C for two hours under static air. The amount of support was calculated to obtain a final nominal metal loading of 1 wt%. The obtained catalysts were labelled Pd<sub>IMP</sub>/CNF-HHT, Pd<sub>IMP</sub>/CNF-LHT and Pd<sub>IMP</sub>/CNF-PS.

**Characterisation of the Pd/CNF catalyst series.** X-Ray diffraction (XRD) data were collected at ambient temperature with a PANanalytical X'PertPRO X-ray diffractometer using Cu K $\alpha$  radiation and operated at 40 kV and 30 mA. X-ray diffraction patterns were recorded between 10 and 80° 2 $\theta$  at a step size of 0.017°. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-alpha<sup>+</sup> spectrometer. Samples were analysed using a monochromatic Al X-ray source operating at 72 W (6 mA  $\times$  12 kV), with the signal averaged over an oval-shaped area of approximately 600  $\times$  400 microns. Data were recorded at pass energies of 150 eV for survey scans and 40 eV for high-resolution scans with a 1 eV and 0.1 eV step size respectively. Charge neutralisation of the sample was achieved using a combination of both low energy electrons and argon ions (less than 1 eV) which gave a C(1s) binding energy of 284.8 eV. The envelopes were fitted after subtraction of a Shirley background<sup>36</sup> using CasaXPS (v2.3.17 PR1.1) with Scofield sensitivity factors and an energy exponent of -0.6. Raman spectroscopy was performed with a Renishaw inVia Raman microscope for analysing the graphitisation degree of the carbon nanofibers. Bare supports, alongside fresh and used catalysts, were analysed. Typically, a sample of approximately 0.01 g was placed on a metal slide inside the spectrometer. The powder was analysed under an Ar<sup>+</sup> laser (514 nm) with an incident laser power of 25 mW. The sample was scanned at an attenuation time of 22 seconds, and 10 scans were carried out to obtain a spectrum. Particle size distributions and mean particle sizes were obtained using transmission electron microscopy (TEM) using a JEOL JEM 2100 TEM operating at 200 kV. Samples for examination were prepared by dispersing the catalyst in high purity ethanol. A drop of the suspension was allowed to evaporate on a holey carbon film supported by a 300-mesh copper TEM grid. The samples were subjected to bright field-diffraction contrast imaging experiments. The mean particle sizes and particle size distributions were determined by measuring the size of over 200 particles from different areas. Scanning electron microscope (SEM) images were taken on

a Hitachi TM3030PLUS equipped with a Quantax70 energy-dispersive X-ray spectroscopy (EDX) to study morphology and determine the palladium content of the samples (fresh and used). The BET surface area was determined from the N<sub>2</sub> adsorption-desorption isotherms in liquid nitrogen at 77 K using a Quantachrome NOVA 2200e instrument. The samples were outgassed for 3 h under vacuum at 227 °C. The total surface area was determined using the BET (Brunauer–Emmett–Teller) equation and the multi-point method.

**Catalytic decomposition of formic acid and analytical methods.** Liquid-phase formic acid decomposition was performed in a two-necked 100 mL round-bottom flask placed in an oil bath with a reflux condenser and a magnetic stirrer at a preset temperature of 30 °C. 10 mL of aqueous HCOOH solution (0.5 M) was placed in the reactor. Upon reaching the temperature, the desired amount of the catalyst was added, and the reaction was initiated by stirring. Each reaction was performed at least twice or thrice to ensure reproducibility. The TOF (turnover frequency number: moles of reactant converted per mol of metal per time unit) has been calculated for a suitable comparison of the initial reaction rates of different catalysts after 5 minutes of reaction. The volume of gas evolved was calculated using the ideal gas law equation:

$$pV = nRT.$$

The initial rate is expressed as the volume produced within the first 5 minutes of reaction.

An approximation of the reaction order was achieved by representing the rate of gas formation *versus* the initial concentration of formic acid, and fitting the data to a power-law model equation:

$$r = kC^n$$

where  $r$  is the reaction rate,  $k$  is the kinetic coefficient,  $C$  is the initial formic acid concentration, and  $n$  is the reaction order.

**Product analysis.** HPLC (High Performance Liquid Chromatography) was used to calculate the concentration of formic acid and therefore the conversion of formic acid during reaction progress. Liquid samples of the reaction mixture were periodically withdrawn, diluted to a 1:100 volumetric ratio with deionised water and analysed by using a HPLC model Agilent 1220 Infinity LC using a column MetaCarb 87H 250  $\times$  4.6 mm, Agilent, at 60 °C and a flow rate of 0.4 mL min<sup>-1</sup>. The instrument is equipped with a Variable Wavelength (VW) Detector pre-set at 210 nm. The eluent was an aqueous solution of phosphoric acid (0.1 wt%). Succinic acid was used as an external standard for the quantification of formic acid.

**Gas analysis.** Using a gas burette as in the water displacement method, the gaseous effluent evolved from formic acid decomposition was collected. Analysis for the detection of H<sub>2</sub> was carried out by using a GC-TCD (Gas Chromatography-Thermal Conductivity Detector CP-3380) equipped with a Poropak Q 6 m  $\times$  1/8" 2.0 mm 80/100 SS column, and using Ar as a carrier gas. CO and CO<sub>2</sub> were quantified using a Varian 450-GC







materials.<sup>35</sup> The component appearing at approximately 284 eV is attributed to the presence of  $sp^2$ -hybridised carbon species, whereas the component at 285 eV to the presence of  $sp^3$ -hybridised carbon species.<sup>60</sup> We observe that both the  $sp^2$  content and the ratio of  $sp^2/sp^3$  increase with increasing annealing temperature as proof of surface graphitisation in agreement with previous reports.<sup>60</sup> For instance, in the case of Pd/CNF-PS this ratio is 2.85–2.98; Pd/CNF-LHT, 3.70–4.13; and for Pd/CNF-HHT, 10.10–10.95, indicating that in CNF-HHT the  $sp^2$  bond is the most abundant. In agreement with this observation, the content of  $sp^3$ -hybridised carbon species decreases as expected with increasing annealing temperature and the deposition of Pd metal nanoparticles has not significantly influenced the observed trend.

Oxygen has been analysed by the O 1s emission (Fig. S5†). O 1s peaks are well described by a Gaussian–Lorentzian curve after Shirley background subtraction. The assignment of the components in the O 1s spectrum is not straightforward. However, there is a certain degree of agreement in the position range of the peaks.

The carbon–oxygen double bond is usually located in the range of 530.0–531.5 eV; regarding the assignment of C–O–H and C–O–C, in the literature several contrasting opinions have been expressed. However, since carbon is slightly more electronegative than hydrogen, carbon–oxygen single bonds in hydroxyl groups should appear at a slightly lower energy, in our case: 531.5–531.8 eV and carbon–oxygen ether-like single bonds at 533.0–533.2 eV; carboxylic groups are usually located in the range of 534.5–535.0 eV and even though the assignment is not clear, the peak at 536.7–537.1 eV might be assigned to adsorbed water.<sup>61–63</sup>

A clear trend when comparing the preparation method is observed for the intensity of the peak attributed to the carbon–oxygen single bonds in hydroxyl groups (C–O–H). The sol-immobilisation method leads to a higher presence of C–O–H compared to C–O–C due to the presence of PVA and its hydroxyl groups as observed in Fig. S5.† As expected, carbon–oxygen ether-like single bonds decrease when increasing the annealing temperature due to the graphitisation of the surface as previously presented.

In summary, XPS analyses have shown a higher concentration of  $sp^2$  hybridisation as a result of increasing the annealing temperature and consequently the graphitisation of the support. The XPS results also indicated that there are two types of Pd species present in the fresh samples. Catalysts prepared by the sol-immobilisation technique exhibit both a higher atomic Pd content and a higher percentage of Pd<sup>0</sup>, since the PVA ligand probably tends to inhibit the oxidation of the Pd surface.

Raman spectroscopy was performed to analyse the structure and graphitisation degree of the carbon nanofibers to a better extent. Raman spectra were measured in the range of 900–1900  $cm^{-1}$ . Fig. 4 and 5 display the Raman spectra of the bare supports and the catalysts subjected to different temperature treatments respectively and Table 2 shows the intensity of the peaks and the  $I_D/I_G$  ratio. The main peaks appear at 1348 and 1572  $cm^{-1}$  and are attributed to the D and G bands of  $sp^2$  clusters respectively. The D band is caused by the presence of



Fig. 4 Raman spectra of the bare supports: CNF-HHT (black curve), CNF-LHT (red curve) and CNF-PS (blue curve).

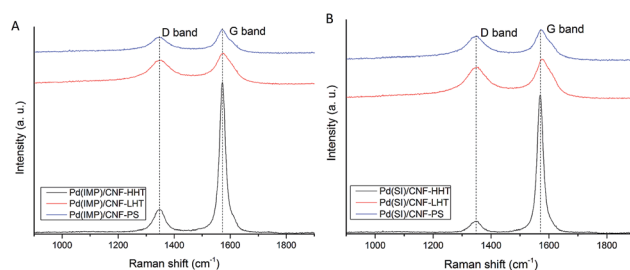


Fig. 5 Raman spectra of the fresh samples. (A) Catalysts synthesised by impregnation: Pd<sub>IMP</sub>/CNF-HHT (black curve), Pd<sub>IMP</sub>/CNF-LHT (red curve) and Pd<sub>IMP</sub>/CNF-PS (blue curve). (B) Catalysts synthesised by sol-immobilisation. Pd<sub>SI</sub>/CNF-HHT (black curve), Pd<sub>SI</sub>/CNF-LHT (red curve) and Pd<sub>SI</sub>/CNF-PS (blue curve).

disorder in  $sp^2$ -hybridised carbon and the G band is due to the stretching of the C–C bonds in  $sp^2$  systems leading to graphitisation. The relative intensity between these two bands ( $I_D/I_G$ ) is related to the structural disorder and subsequently to the size of graphitic domains.<sup>64</sup> All the Pd/CNFs studied in this work present both D and G Raman bands. For the bare supports, as expected, the  $I_D/I_G$  ratio decreases with increasing annealing temperature, presenting a more significant drop when the support is treated at the highest temperature. This should be the trend observed for the catalysts as well. However, we observe a lower than expected  $I_D/I_G$  ratio for the catalysts supported on CNF/PS (Fig. S6†). This fact gave us a hypothesis to consider: during the preparation method, the catalyst was washed to remove the remaining stabiliser or metal precursor impurities and this could have affected the amorphous phase of the carbon, being washed away to some extent and subsequently showing this low  $I_D/I_G$  ratio.

In order to prove this hypothesis, the bare support was treated with water for 1 hour under stirring and dried after filtration under the same conditions as the previous samples. The Raman spectrum of the dried sample showed a further decrease in  $I_D/I_G$ : 0.61 for Pd<sub>IMP</sub>/CNF-PS and 0.67 for Pd<sub>SI</sub>/CNF-PS, confirming the fact that the amorphous carbon was removed to a certain extent from the surface when preparing the catalyst. The difference observable between the concentrations



of  $sp^2$  and  $sp^3$  from XPS for the catalysts is in agreement with the results obtained from Raman; the catalysts annealed at 3000 °C present the highest graphitisation and a big difference with LHT samples (annealed at 1500 °C) as observable in the  $sp^2/sp^3$  ratio. Between LHT and PS samples there is a small difference confirmed by both the concentrations of  $sp^2$  and  $sp^3$  and the  $I_D/I_G$  ratio.

The particle size distributions of the catalyst series for both impregnated and sol-immobilised samples were assessed from the analyses of bright field TEM micrographs. The samples synthesised *via* the impregnation route (Fig. 6) present a particle size distribution in the 2.5–10 nm range, with an average particle size of 5.9 nm, and those catalysts prepared by the sol-immobilisation method present a narrower particle size distribution of 2–8 nm (Fig. 7) and a smaller average particle size of 4.2 nm.

Table 3 shows the mean particle size of the as-synthesised fresh and used catalysts. Fig. S7 and S8† present the representative TEM micrographs and particle size distribution for the used catalysts. No remarkable increment in the particle size has been observed for the used catalysts. TEM analyses provide evidence that the Pd nanoparticles were more evenly dispersed on the catalysts prepared by sol-immobilisation in comparison with the impregnated samples. Regarding graphitisation, it is remarkable how the particle size tends to decrease for the

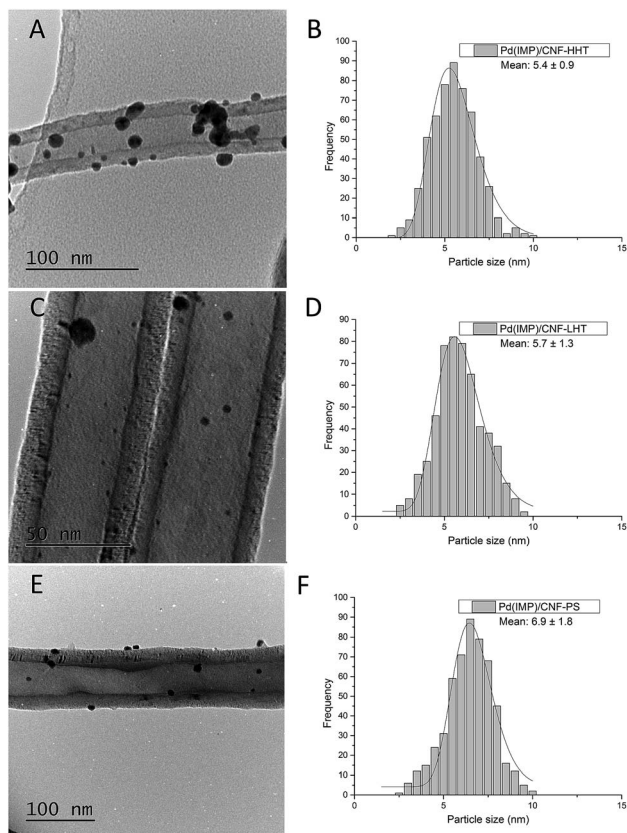


Fig. 6 Bright field TEM micrographs and corresponding histograms of the particle size distributions for the fresh catalysts prepared by impregnation. (A and B) Pd<sub>IMP</sub>/CNF-HHT, (C and D) Pd<sub>IMP</sub>/CNF-LHT, and (E and F) Pd<sub>IMP</sub>/CNF-PS.

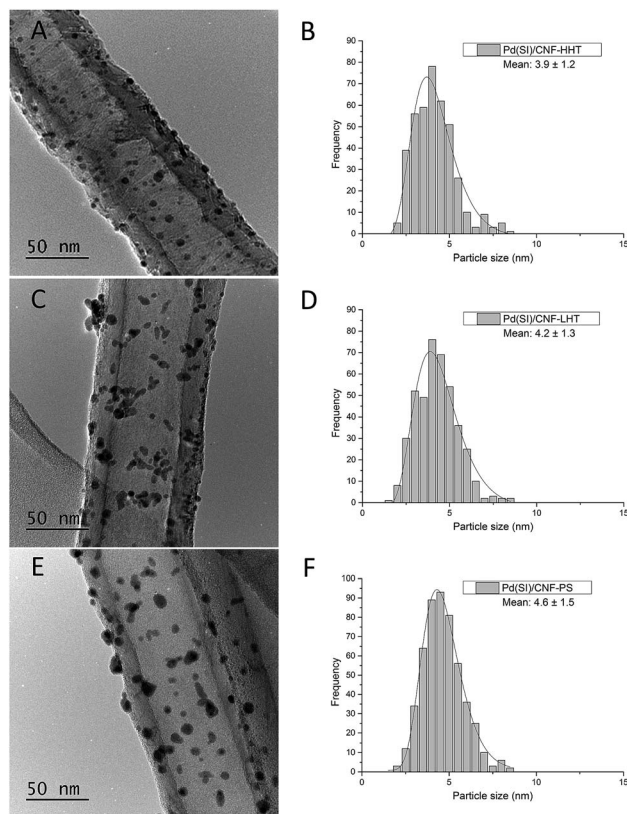


Fig. 7 Bright field TEM micrographs and corresponding histograms of the particle size distributions for the fresh catalysts prepared by sol-immobilisation. (A and B) Pd<sub>SI</sub>/CNF-HHT, (C and D) Pd<sub>SI</sub>/CNF-LHT, and (E and F) Pd<sub>SI</sub>/CNF-PS.

catalysts whose support has been treated at increasing annealing temperature. The concentration of  $sp^2$  could explain this behaviour and  $sp^3$  carbon previously calculated. Carbon with  $sp^2$  hybridisation is less reactive than carbon with  $sp^3$ . The catalysts supported on CNF-HHT present a high percentage of  $sp^2$ , which means that less reactive sites are present on the carbon surface. During the preparation method, sol-immobilisation or impregnation methods, the nanoparticles bind to the nanofiber preferentially by the most reactive sites of carbon ( $sp^3$ ). This could facilitate a smaller particle size for HHT-CNF since the concentration of  $sp^3$  sites is lower and supposedly, these sites will be distributed more spatially within the nanofiber.

The distribution and dispersion of Pd within the Pd/CNF catalysts were evaluated with SEM-EDX. Fig. 8 displays a typical SEM image of the fresh and used Pd<sub>IMP</sub>/CNF-HHT. No significant variation is appreciable between the fresh and the used samples. To deeply characterise the catalysts using this technique, EDX analysis on a large area during SEM observation was performed confirming the presence of Pd. Total metal loading derived from the EDX analysis for both fresh and used catalysts series is presented in Table 4. The total metal loading of the as-synthesised catalysts approaches the theoretical value of 1 wt%, and it is not considerably affected by the preparation method used in this work.









Fig. 10 Potential energy surface for formic acid decomposition on (A) Pd(111), (B) Pd(011) and (C) Pd(001) surfaces. Red and blue lines indicate HCOO and COOH paths respectively. The solid lines lead to CO<sub>2</sub> whereas the dashed line to CO.

H<sub>2</sub> (**1a**) because the C–O dissociation step (**1b**) is even more unfavourable (+1.12 eV) for (011) than for the (111) surface and thus, CO evolution is largely avoided.

**(001) Surface.** The adsorption of *trans*-HCOOH supposes a relaxation of  $E_B = -0.80$  eV and the breakage of the O–H bond ( $E_R = -0.25$  eV). The separation of hydrogen and the splitting of C–H stabilise the system by 0.30 eV. After the re-orientation of HCOOH to *cis* and the C–H scission ( $E_R = -1.55$  eV), the hydrogen separation destabilises the carboxylic species by 0.04 eV. In this case, the C–O dissociation step (**1b**) is still unfavourable, but the value is much lower compared with the other two surfaces (+0.33 eV). Besides this, O–H spillover, the last step in **2b** is just slightly unfavourable compared as well with (011) and (111) where it certainly needed more energy. Due to these two facts, (001) is the surface that can lead to a higher concentration of CO since its evolution is not as unfavourable as in (011) and (111).

Since **1a** (*via* HCOO) is the main pathway followed by formic acid decomposition, according to Fig. 10, it is clear that for both (111) and (011) surfaces, this pathway is exothermic. On the other hand, for the (001) surface, pathway **1a** finds two steps in

which absorption energies increase, having a negative impact on the catalyst activity. In fact, the last step in pathway **1a**, the H spillover, on the (001) has a potential energy of  $E_R = -1.38$  eV, while on the (111) surface  $E_R = -1.41$  eV and on (011)  $E_R = -1.49$  eV. Hence, the resulting energy of the system is higher for the (001) surface and therefore, we can conclude that very small nanoparticles with a large extensive area of the (001) surface would be detrimental to both catalyst activity and CO evolution. In our investigation, we have presented the maximum activity for the catalysts with a mean particle size of approximately 4 nm. This diameter seems to be large enough to avoid the (001) surface to a large extent.

Taking into account the observed catalytic and potential energy surface trends, the catalytic activity increases with the increase of (111) and (011) surfaces, and furthermore, it is evident that the *cis* configuration is the pathway (**2a**) that leads to CO formation even at low temperature is particularly enhanced in the case of the (001) surface. Therefore, it is crucial to design experimental methodologies to develop supported Pd nanoparticles exposed with a higher degree of (111) and (011) surfaces.

## Conclusions

A series of monometallic Pd nanoparticles supported on several carbon nanofibers (CNFs) were synthesised. Three CNFs with different graphitisation grades were used. Sol-immobilisation and impregnation techniques were selected as model preparation methods widely used for the deposition of Pd nanoparticles.

Pd/CNFs prepared by the sol-immobilisation method exhibit higher catalytic activity when compared with catalysts prepared by the impregnation method due to (i) the higher surface atomic Pd percentage, (ii) higher percentage of Pd<sup>0</sup> and (iii) smaller Pd particle size. Probably, the sol-immobilisation method tends to distribute Pd metal nanoparticles on the surface of the nanofibers, whereas the impregnation method leads to a partial filling of the nanofibers and distribution of Pd nanoparticles in the inner wall, besides the distribution on the outer CNF surface.

The heat treatment on CNFs affects catalyst activity. The catalytic performance of the samples significantly increases with the increase of annealing temperature. A heat treatment at 1500 °C did not significantly modify the surface properties of CNFs. In contrast, treating CNFs at 3000 °C rearranges the structure improving the order and the degree of graphitisation. This increase of activity with annealing temperature has been attributed to the presence of smaller Pd nanoparticles formed and improved dispersion. A TOF of 979 h<sup>-1</sup> was achieved by Pd<sub>51</sub>/CNF-HHT, the most active catalyst in this series, with high selectivity for H<sub>2</sub> (>99%) under mild reaction conditions, *e.g.* 30 °C. Finally, DFT studies provide valuable insights into the role of under-coordinated sites in terms of activity and preference of reaction pathways toward CO<sub>2</sub> and H<sub>2</sub> evolution against CO formation and provide answers to the important question of how to avoid/minimise the formation of CO. (001) was found to be the surface in which CO would evolve at faster rates





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