



Pd nanoparticles supported on N-doped nanocarbon for the direct synthesis of H₂O₂ from H₂ and O₂

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Abstract

Pd nanoparticles deposited by sol-immobilization on N-doped nanocarbon (carbon nanotube-like from Pyrograf Products; N-CNT-like) is studied in the direct synthesis of H₂O₂ and compared with those of the undoped catalysts or prepared by the same Pd deposition method on active carbon (Vulcan XC-72) as the support. The catalytic tests were carried out using a slurry batch- or semi-continuous reactor at room temperature and a total pressure of 10 bar using CO₂-expanded methanol as the solvent. The Pd on N-CNT-like gives high productivities to H₂O₂, comparable to the best literature results, while the selectivity to H₂O₂ is low due to the low oxygen partial pressure and likely low oxygen coverage on Pd particles. The introducing of nitrogen in the CNT-like material favors not only the dispersion of Pd (with a consequent improvement of the activity), but also the specific turnover, due to probably the electronic effect of pyridine-like nitrogen sites present in the N-CNT-like support favoring the O₂ surface coverage. However, the introduction of these N functionalities on the surface has also a negative effect on the rate of H₂O₂ consecutive conversion to water.

Keywords: hydrogen peroxide, Pd, nanocarbon, CNT-like, H₂O₂ direct synthesis

1. Introduction

The direct synthesis of H₂O₂ from H₂/O₂ is increasing of interest with the starting of operations of new large scale processes using H₂O₂ as the oxidant: synthesis of caprolactame and propene oxide [1]. One major problem in the direct synthesis of H₂O₂ derives from the need to operate with diluted H₂ and O₂ gaseous feeds to be outside the explosion range of the O₂/H₂/inert mixture, with consequent low productivities. In order to overcome this problem, high pressure operations (ca. 10 MPa) are typically reported in most of the patents [2], [3] and [4].

The reaction of direct synthesis of H₂O₂ using Pd-based catalysts is known from long time. In the 80s it was an intense research activity in many companies on this reaction [4], but after the explosion of a pilot-scale reactor at DuPont the research declined. In the last 5–10 years, a return of interest on this reaction from both companies and academic groups derived from the need of using cleaner

oxidation reactants, and reduce the environment impact of various large scale processes, such as those indicated above and the direct benzene hydroxylation to phenol [1]. Although most, but not all, of the more recent studies have been made using low H₂ concentrations (close to lower explosivity limit of the H₂:O₂:inert mixture), still major safety problems remain. In fact, high selectivities in the reaction require to use large O₂ to H₂ ratios and organic solvents, between which methanol is one of the most common. In these conditions, e.g. using volatile organic solvents such as the alcohol, high oxygen concentrations and pressures, the mixture is still potentially explosive. Industrial operations using large reactors are thus potentially unsafe, even if considering technical advances in reactor safety design. In addition, the cost of operations with high pressure significantly reduces the potential economic advantage of the direct synthesis of H₂O₂ with respect to the commercial antraquinone route.

In the past, we explored the possibility of using catalytic membranes/diffusers for intrinsically-safer operations in the direct synthesis of H₂O₂ [5], [6], [7] and [8]. The limit, however, was the low overall productivity (per reactor volume) and high cost of the membrane.

An alternative approach for intrinsically-safer operations is to use microchanneled reactors, where the high surface to volume ratio allows an effective quenching of radical-chain reactions, thus allowing operating safely inside the explosivity range. This solution is particularly suited for small-scale applications.

One of the limits still present in the use of microreactors is that they require the development of new catalysts. The first motivation is that the catalyst in powder form, such as used in the slurry-type reactor typically adopted in most of the studies, cannot be used due to microchannels plugging problems. The deposition of a thin film on the microchannels walls is not optimal in terms of amount of catalyst and fluidodynamic aspects, particularly for gas-liquid reactions such as the case of the H₂O₂ direct synthesis. In wall-coated microchannels, Reynold number may be not enough to guarantee good turbulence or Taylor flow regimes may establish. If the catalyst is instead present in the form of nanofibres filling the void space of the microchannels, the potential advantages are: (i) better wall-to-volume ratio (more effective quenching of radical-type explosive reactions), (ii) increase in the surface to volume catalyst ratio (reduced mass transfer limitations which favor decomposition of H₂O₂), (iii) increase in the catalyst loading per volume of microreactor, (iv) increase in the microturbulence (better performances and safety), (v) reduced problems related to gas cap over the catalyst surface.

The use of the catalyst in the form of nanofibres filling the void space of the microchannels has thus many advantages in terms of reactor design.

Several types of supports (acid oxides, resins, mesoporous materials) have been reported in literature [2], [3] and [4], but essentially no data on the use of carbon nanotubes or similar materials are given.

Nanocarbon materials (nanofibres, nanotubes, etc.) are the natural choice as support to prepare 1D-type catalysts suitable for use in microchanneled reactors. The aim of this work is thus an exploratory investigation on the use of carbon nanotube like (CNT-like) materials as a support for Pd nanoparticles in the direct H₂O₂ synthesis and the analysis of the effect of modification of the surface properties of the CNT-like support by doping with nitrogen via gas phase amination.

Tests were made at lower pressure (1 MPa) than that typically reported in patents or literature data (in the 4–10 MPa range), because low pressure operations are a target for microchanneled reactors to reduce the costs of operations. However, to simplify the study and have results more comparable with literature, catalytic tests have been made in batch- or semi-continuous autoclave reactors. Catalytic tests have been made in the presence of CO₂ as ballast, because as shown earlier [1] and [10], the presence of CO₂ modifies the properties of the solvent (methanol)

improving in particular the solubilization of oxygen. We refer for this reason as CO₂-expanded methanol as the solvent.

2. Experimental

Commercial carbon nanotube-like materials used in this study have been supplied by Pyrograf Products, Inc. The nomenclature used by the company, PR24PS, refers to the specific grade, PS stays for “Pyrolytically Stripping” which is the post-treatment applied to the as-produced nanotubes-like materials in order to remove the polyaromatic hydrocarbons from the surface. Scanning electron micrograph (SEM) images show morphology of the fibres with an average diameter of 88 ± 30 nm. Although a carbon nanotube (CNT) structure is present, we prefer to indicate these materials as CNT-like, because high-resolution transmission electron images show that the inner layer is composed of angled graphite sheets, e.g. “herringbone” morphology [11]. The external layer is instead due to deposited pyrolytic carbon, so called turbostratic graphite. The general morphological characteristics of this nanocarbon are thus similar to carbon nanotubes (CNTs), but the effective nanostructure is different. This sample is indicated hereinafter as CNT-like. These nanocarbon materials are available in relative large amounts at low cost, and they are thus a good suitable choice to develop the aimed catalysts for H₂O₂ direct synthesis. The presence of catalyst impurities was determined by X-ray fluorescence. Only traces of Fe and S and in very low amounts Mg, Cl, Ca and Cr are present. The surface area, determined by full BET method, is $55 \text{ m}^2 \text{ g}^{-1}$ and a dominant macroporous texture is present.

N-doped CNT-like support was prepared by post-synthesis treatment of the pristine CNT-like by using NH₃ flow (0.2 L min^{-1}) at 873 K for 4 h. Before this procedure, the CNT-like was pretreated with nitric acid (20 g of CNTs per liter of HNO₃) at 373 K for 2 h under continuous stirring. Then they were rinsed until the washing water turns on neutral pH. The sample was then dried at 343 K overnight. This sample is indicated hereinafter as N-CNT-like. The nature of nitrogen functionalities on the CNT-like surface, and its graphite structure, were evaluated by XPS synchrotron radiation [12] as well as by elemental analysis (Leco TC-300/EF-300 N/O analyzer). The amount of N introduced after treatment with ammonia at 873 K is 1.1 wt% as bulk value, and about 8% on the surface.

The palladium was then deposited on CNT-like and N-CNT-like using sol-immobilization procedure [13]. Na₂PdCl₄ (0.093 mmol) was dissolved in 100 ml of H₂O, and PVA (poly vinyl alcohol) was added to the solution in the Pd/PVA (w/w) ratio of 1:1. The solution was stirred for 5 min, after which 0.37 mmol of NaBH₄ was added under vigorous magnetic stirring. The brown Pd(0) sol was formed immediately. The sol was immobilized by adding the support (acidified at pH 2 by sulphuric acid) under vigorous stirring. After 30 min the slurry was filtered and the

catalyst washed thoroughly with distilled water and dried at 353 K overnight.

In addition to CNT-like and N-CNT-like, a reference acid, graphitic and low surface area active carbon (Vulcan XC-72 from Cabot; surface area, 254 m² g⁻¹; average particle diameter, 30 nm; 0.3%, sulphur) was used as the support. The characteristics of this active carbon make it a suitable type of material for the comparison with CNT-like materials. This sample is indicated hereinafter as C.

The wt% of the metal deposited on the support after the preparation was determined by atomic absorption spectroscopy (AAS) performed with a Perkin-Elmer Analyst 200 apparatus. Samples for analysis were prepared dissolving 20 mg of the dried catalyst in an aqua regia solution. The amount of Pd in the samples was respectively 0.90 wt% and 0.91 wt% for Pd/CNT-like and Pd/N-CNT-like catalysts, while 3 wt% for Pd/C. A further reference sample was prepared by incipient wetness impregnation using γ -Al₂O₃ SasolPuraloxSCCa-30/200 as the support. The amount of Pd was 2.7 wt%. This sample is indicated hereinafter as Pd/A.

Palladium particles morphology, size distribution and dispersion, were determined by transmission electron microscopy and statistical analysis. HRTEM investigations have been carried out with a Philips CM200 TEM FEG. The samples were dry-deposited on a holey carbon film supported on a Cu grid.

All catalysts were tested at room temperature in the catalytic oxidation of H₂ to H₂O₂ in a stirred stainless steel reactor coated with Teflon (capacity 300 ml) containing 30 mg of catalyst in a fine powder form and 125 ml of anhydrous CH₃OH as a reaction medium, in order to improve both solubility of H₂ and particularly O₂. Two hundred and fifty microliter of H₂SO₄ were added for H₂O₂ stabilization as reported in previous papers [4] and [5]. Batch- and semi-batch operations (e.g. continuous feed of the gas to the batch slurry reactor containing the solvent) tests were made. In batch-type tests, a gas mixture containing 10 vol% of H₂ with a H₂/O₂ ratio of 1:2 and 50% CO₂ was bubbled continuously through the reaction medium at room temperature until the pressure reaches the set value of 1 MPa, after which the feed was stopped. These conditions permit to work outside the explosion range of H₂/O₂ mixtures. In semi-batch tests, the gas feed was continuous during the experiments. Stirring (1300 rpm) was started after reaching the desiderate pressure, and experiments were carried out for 90 min (batch operations) or longer times (semi-continuous operations). Data were corrected to take into account the initial mixing time. Gas analysis for H₂ and O₂ was performed using a gas chromatograph unit (Agilent 3000 A equipped with a Molsieve 5 Å column using argon as carrier gas). Conversion of H₂ was calculated by gas analysis before and after reaction. The reaction products were analysed by potentiometric titrations of H₂O₂ (Metrohm, 794 Basic Trino) and H₂O (Metrohm, 831 KF Coulometer), respectively.

Tests in H₂O₂ decomposition were analogous to those of direct synthesis (batch reactor), but introducing

already a methanol solution containing a determined amount of H₂O₂ and using a gas feed in which O₂ was substituted with N₂. These tests were also made at room temperature.

3. Results and discussion

3.1. Catalytic performances

Reported in Fig. 1 is the behavior of the three catalysts in the direct synthesis of H₂O₂ in a batch (Fig. 1(a) and (c)) and semi-batch (Fig. 1(b) and (d)) reactor. Data are reported in terms of amount of H₂O₂ formed per mg of Pd (Fig. 1(a) and (b)) as a function of time, or in terms of H₂O₂ concentration (wt%) as a function of time (Fig. 1(c) and (d)).

The results of the tests in batch conditions show total consumption of H₂ after about 1 h and thus all catalysts arrive to a maximum formation of H₂O₂ (in the 1.4–1.8 wt% range). The value depends on the selectivity in H₂O₂ formation which varies from about 45% for Pd/C and Pd/N-CNT-like catalysts to 35% for Pd/CNT-like sample. In terms of specific activity per amount of Pd, the behavior of Pd/CNT-like and Pd/C is similar (initial rate, e.g. in the first half hour of reaction), while the Pd/N-CNT-like shows a 2–3 times higher rate.

These results and order of reactivity are confirmed in the semi-batch reactor tests, but in this case no plateau in the formation of H₂O₂ is observed, because the feed of the H₂/O₂/CO₂ gas mixture is continuous. In this case a linear increase in H₂O₂ concentration is obtained, with only a slight deviation at the higher H₂O₂ concentrations for the CNT-like based sample. This result shows that, within the limits of this type of experiments, there is no deactivation of the sample and no significant deviation of the catalyst productivity on increasing the concentration of the H₂O₂ formed. In other words, these results pointed out the potential applicability of this type of catalysts for microchanneled-type continuous reactors, although further tests are necessary. In agreement with the absence of deactivation, the analysis of the reaction solution after the catalytic tests by atomic absorption spectroscopy evidences the absence of detectable leaching of Pd, differently from recent literature results [14] showing a large metal leaching over carbon-based catalysts. After filtration and drying, the catalyst could be reused with reproducible results.

Table 1 reports the catalyst productivity and selectivity determined for the studied catalysts and for comparison selected literature results (from open literature and patents). The reaction conditions in terms of hydrogen and oxygen partial pressure, and total operative pressure are also reported. To note that data in this work and those in [16] were obtained using CO₂ as ballast, while other results were obtained using N₂ as ballast. The reaction temperature ranges from 279 K [20] to 313 K [17], while is room temperature in the other cases. Some differences also exist in

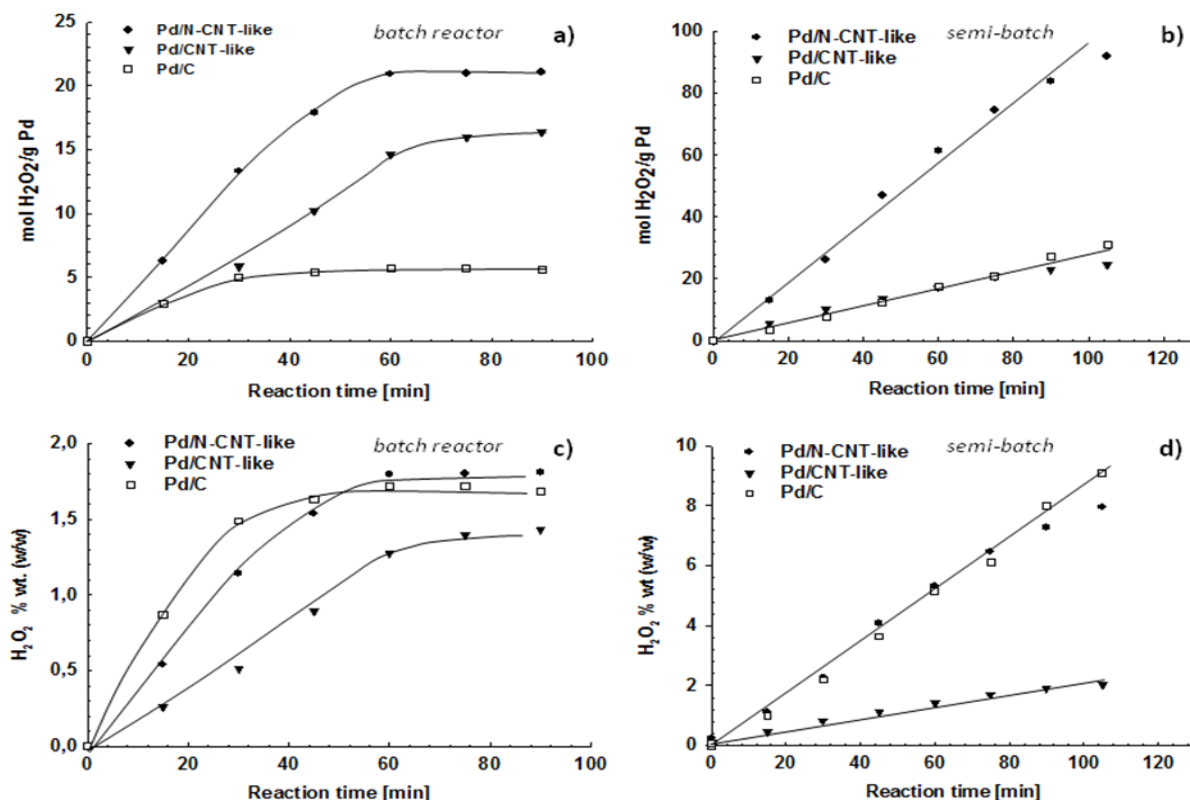


Fig. 1: Catalytic behavior of Pd/CNT-like, Pd/N-CNT-like and Pd/C catalysts in the direct synthesis of H₂O₂ in batch- and semi-batch type reactor. See text for experimental conditions.

Table 1: Catalyst productivity in the direct synthesis of H₂O₂ and comparison with selected literature results.

| Catalyst | Mol H ₂ O ₂ /(kg _{cat} h) | Selectivity H ₂ O ₂ % | P _{H₂} , MPa | P _{O₂} , MPa | P _{Tot} , MPa | Ref. and notes |
|--|--|---|----------------------------------|----------------------------------|------------------------|----------------|
| 0.9% Pd/N-CNT-like | 128 | 45 | 0.1 | 0.2 | 1 | This work |
| 0.9% Pd/CNT-like | 98 | 35 | | | | |
| 3% Pd/C | 112 | 43 | | | | |
| 2.5% Pd/C | 42 | - | 0.13 | 0.26 | 3.7 | [16] |
| 2.5% Au/2.5% Pd/C | 110 | - | | | | |
| 1.5% Pd on sulphonic acid polystyrene resins | 70 | 77 | 0.2 | 4.8 | 10 | [17] |
| 0.6% Pd/carbon black | 49 | 99 | 0.33 | 2.31 | 11 | [18] |
| 2.4% Pd/0.1% Au/Al ₂ O ₃ | 12 | - | 0.15 | 1 | 5 | [19] |
| 0.9% Pd/0.1% Pt/carbon | 8 | 83 | 0.36 | 1 | 10 | [20] |

Table 2: Effect of the total pressure and use of CO₂ as ballast on the catalyst activity and selectivity in H₂O₂ direct synthesis. Catalyst: Pd/A, batch reactor.

| Inert as ballast | Total P, MPa | | | |
|---|-----------------|----------------|-----------------|----------------|
| | 0.65 | | 0.9 | |
| | CO ₂ | N ₂ | CO ₂ | N ₂ |
| Mol H ₂ O ₂ /g Pd h | 1.18 | 0.35 | 1.59 | 0.41 |
| Selectivity H ₂ O ₂ % | 30 | 10 | 39 | 11 |

Table 3: Surface area and mean diameter of Pd nanoparticles (estimated from HRTEM data) and specific rate of H₂O₂ formation per m² of Pd surface area in the studied catalysts.

| | Pd, wt% | Average diameter Pd particles, nm | Surface area Pd particles | | mol H ₂ O ₂ /m ² Pd h |
|---------------|---------|-----------------------------------|----------------------------------|----------------------|--|
| | | | m ² /g _{cat} | m ² /g Pd | |
| Pd/CNT-like | 0.90 | 3.6 | 1.25 | 138.6 | 4.95 |
| Pd/N-CNT-like | 0.91 | 2.7 | 1.68 | 184.8 | 8.58 |
| Pd/C | 3.01 | 3.9 | 3.84 | 128.0 | 4.75 |

terms of type of reaction, and presence of additives, as well as amount of H₂O₂ formed, besides to type of catalyst as indicated in Table 1.

On the other hand, a more homogeneous comparison is not possible. Within these limits, however, it may be concluded that the productivity obtained by our CNT-like based catalysts is rather high, also taking into account the mild reactions conditions, particularly in terms of low oxygen partial pressure, as well as total operative pressure.

Data reported in Table 1, however, evidence a significant lower selectivity to H₂O₂ in our samples. The issue is whether this is a consequence of the reaction conditions used and in particular the low pressure, or instead a specific (negative) characteristic of our samples. As indicated before, the target of our experimentation was to use low pressures (<1.5 MPa) and thus higher pressure operations were not useful from this point of view. Other Pd-based catalysts we tested gave typically even lower selectivities to H₂O₂.

Reported in Table 2 is the effect of the total pressure and use of CO₂ or N₂ as the ballast in the direct synthesis of H₂O₂, although using alumina as support for Pd, to evidence the influence of the support on the productivity to hydrogen peroxide which results about 40 times lower than that of Pd/N-CNT-like catalysts in terms of activity per Pd amount and about 15 times lower in terms of activity per catalyst amount. Selectivity to H₂O₂ is instead comparable, evidencing that there is no relationship between selectivity and productivity of the catalysts. The data in Table 2 also evidence that increasing the total pressure, at equivalent composition of the feed, not only there is an increase in the productivity, but also in the selectivity. The use of CO₂ as the ballast significantly increases both the productivity and the selectivity. The effect was similar also on other type of supports [10] and was interpreted as deriving from the effect of total pressure and of CO₂ in the modification of the amount of dissolved oxygen and thus, as a consequence, on the surface coverage by oxygen of Pd particles. Working at room temperature we can exclude the oxidation effect of CO₂.

The effect of CO₂ was also observed in other reactions of oxidation such as the p-xylene oxidation to terephthalic acid and interpreted as equilibrium between CO₂ and peroxocarbonate species which enhances the amount of solubilized oxygen in methanol [1] and [15]. Increasing the oxygen partial pressure it is thus reasonable to obtain higher selectivities to H₂O₂. The lower selectivity to hydrogen peroxide we observed (Table 1) is mainly in relation to the effect of the different oxygen partial pressure in the different open literature and patent results. On the other hand, this indicates that, from the practical point of view, to operate at low total and oxygen partial pressure it is necessary to find an additive which might further promote oxygen solubility in the solvent, in order to increase the selectivity to H₂O₂.

3.2. Role of the doping with nitrogen of CNT-like support

Data reported in Fig. 1 clearly evidence a superior specific activity (per amount of Pd) of the N-CNT-like with respect to either pristine CNT-like and graphitic-type carbon. In order to analyze whether this aspect is related to only a better dispersion of Pd particles or on additional factors, we have characterized the samples by high-resolution transmission electron microscopy (HRTEM). Reported in Fig. 2 are HRTEM images of Pd/N-CNT-like and Pd/CNT-like and the distribution of particle diameters determined by statistical analysis of the images. The average diameter of the Pd particles is 2.7 nm and 3.6 nm for Pd/N-CNT-like and Pd/CNT-like samples, respectively. In Pd/C a slightly broader distribution (from about 2 nm to 8 nm sizes) with average value at 3.9 nm was observed. There is thus an influence of the support on the average diameter of the particles, although not very marked.

Reported in Table 3 is the average diameter of Pd particles in the different samples and the surface area of Pd particles which may be estimated from HRTEM data per amount of catalyst or amount of Pd. Using these data and those reported in Fig. 1, it is possible to determine the specific activity of the various samples in the direct synthesis of H₂O₂ per m² of surface of Pd (Table 3). Similar results are obtained for Pd/CNT-like and Pd/C samples, indicating that thus for these samples the different specific activities are only related to the amount and dispersion of Pd. On the contrary, this specific (turnover-like) activity is around twice that of the other samples. This result evidences that the presence of nitrogen functionalities in the CNT-like material introduces not only a better dispersion of Pd (lower average diameter), but also an effective increase of the specific activity of Pd particles.

In order to better understand the type of nitrogen functional groups present on the surface, the N-CNT-like sample was studied by XPS (synchrotron radiation) in the N 1s core level region. The amination at 873 K of oxidized CNT-like sample introduces N functionalities in the graphitic-like structure of the CNT-like material as shown in the N 1s-XPS spectrum reported in Fig. 3. More results on the nature of N functionalities present in these samples were earlier reported [12]. To this work is made reference regarding the details of the deconvolution of the N 1s spectrum. Four different chemical bonding configurations of N in this sample could be identified. The pyridine-like nitrogen region (labeled as N1 at about 398.5 eV) is referred to N atoms contributing to the π system with one electron; the pyrrol-like N region (labeled as N2 at about 400.1 eV) is referred to N atoms contributing to the π system with two electrons such as lactam and pyrrol species; the third region is referred to the quaternary nitrogen (labeled as N3 at about 401.1 eV), including protonated pyridine and substitutional nitrogen where the N replaces a C atom in the graphitic structure. The fourth region (labeled as N4 at

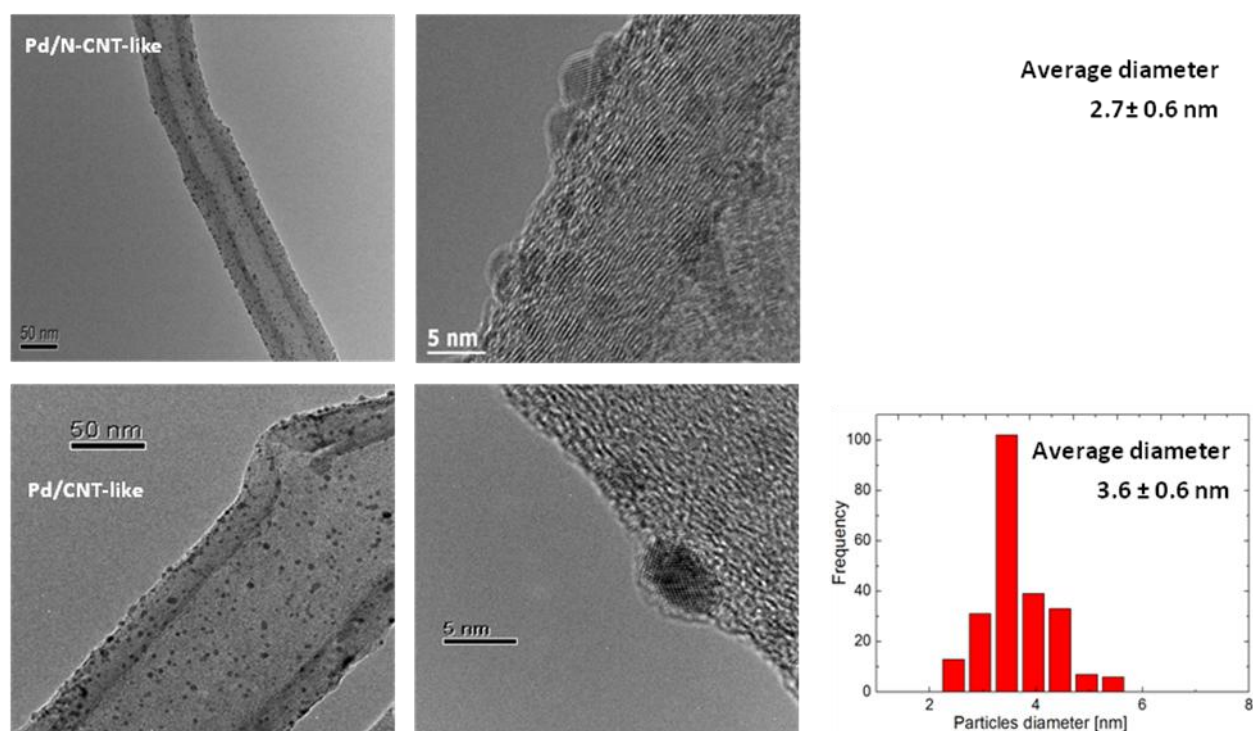


Fig. 2: HRTEM images of Pd/N-CNT-like and Pd/CNT-like samples, and relative distribution of Pd particles.

about 403.4 eV) is attributed to the N–O bond in pyridine oxide species. Based on these results, it is possible to indicate that the most abundant species present in N-CNT-like sample is a N species in a pyridine like fashion which shows high Lewis basic character.

It is thus reasonable to consider that the presence of these surface N functional groups will have not only a positive effect in stabilizing smaller Pd nanoparticles (improving Pd dispersion probably acting as Lewis basic sites on the CNT-like surface and producing localized charge accumulation on the carbon surface which can act as coordinative site for very small Pd nanoparticles), but also an electronic effect on Pd nanoparticles. Studies to better analyze this aspect are in progress, but it may be tentatively suggested that more electron-rich Pd nanoparticles would favor O₂ surface coverage and the rate of H₂O₂ synthesis. Based on this interpretation, it may be expected, however, that also selectivity would be better in Pd/N-CNT-like sample, differently from what observed (Table 1).

The presence of these N functionalities, however, also affects the surface acidity and this may have a role on the rate of H₂O₂ decomposition. Zeta potential measurements show a shift from a pH of about 2.4 in the PZC (point zero charge) of pristine CNT-like to a pH of about 4.4 in N-CNT-like sample. In order to check whether this change in the surface acidity and, in general the presence of N functional groups, would affect the rate of H₂O₂ consecutive conversion to water, tests of hydrogen peroxide decomposition have been made on Pd/CNT-like and Pd/N-CNT-like samples. The results are reported in Fig. 4.

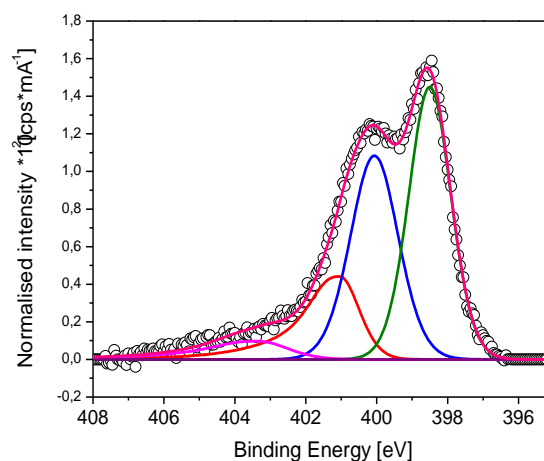


Fig. 3: XPS spectrum (synchrotron radiation) in the N 1s core level region of N-CNT-like sample. See text for spectral deconvolution.

As described in Section 2, these tests were similar to those of H₂O₂ synthesis, except that oxygen is substituted with nitrogen, and hydrogen peroxide is already present at the start of the reaction. In these tests it is thus possible to evaluate the combined rate of hydrogenolysis and decomposition of H₂O₂. Note that during the catalytic reaction, the presence of oxygen would limit the rate of hydrogenolysis, and thus the rate measured in these tests is probably proportional, but not equivalent to that present during the synthesis of H₂O₂. As noted earlier [1] and [4], the H₂O₂

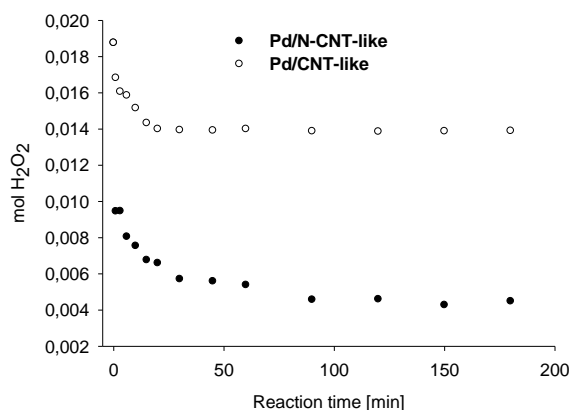


Fig. 4: Tests of H₂O₂ hydrogenolysis and decomposition on Pd/CNT-like and Pd/N-CNT-like samples.

hydrogenolysis is one of the main pathways responsible of selectivity lowering in the synthesis of H₂O₂ and it is thus necessary to make tests in the presence of H₂ to obtain indications on the relative relevance of consecutive reactions of H₂O₂ conversion to water in the different catalysts.

The results reported in Fig. 4 clearly evidence that the rate of H₂O₂ hydrogenolysis/decomposition using Pd/N-CNT-like sample is largely higher than that using Pd/CNT-like. The behavior of Pd/C was found similar to that of Pd/CNT-like. These results thus indicate that probably the intrinsic selectivity in Pd/N-CNT-like sample, e.g. the rate between the two parallel reactions of oxidation of hydrogen to hydrogen peroxide or water, is higher, but also higher the rate of consecutive conversion of H₂O₂ to water. This interpretation could explain why the presence of N functionalities in CNT-like material improves the specific activity (turnover-like) of supported Pd particles, while does not improve the selectivity. However, further studies are necessary to better understand this question.

4. Conclusion

As described in Section 2, these tests were similar to those of H₂O₂ synthesis, except that oxygen is substituted with nitrogen, and hydrogen peroxide is already present at the start of the reaction. In these tests it is thus possible to evaluate the combined rate of hydrogenolysis and decomposition of H₂O₂. Note that during the catalytic reaction, the presence of oxygen would limit the rate of hydrogenolysis, and thus the rate measured in these tests is probably proportional, but not equivalent to that present during the synthesis of H₂O₂. As noted earlier [1] and [4], the H₂O₂ hydrogenolysis is one of the main pathways responsible of selectivity lowering in the synthesis of H₂O₂ and it is thus necessary to make tests in the presence of H₂ to obtain indications on the relative relevance of consecutive reactions of H₂O₂ conversion to water in the different catalysts.

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