Pd nanoparticles supported on N-doped nanocarbon for the direct synthesis of H_2O_2 from H_2 and O_2

S. Abate [a], R. Arrigo [b], M.E. Schuster [b], S. Perathoner [a,*], G. Centi [a], A. Villa [b], D. Su [b], R. Schlögl [b]

[a] Dipartimento di Chimica Industriale ed Ingegneria dei Materiali (INSTM, UdR Messina, CASPE), University of Messina, Salita Sperone 31, 98166 Messina, Italy
[b] Department of Inorganic Chemistry, Fritz-Haber Institut der Max Planck Gesellschaft, Berlin, Germany

ABSTRACT

Pd nanoparticles deposited by sol-immobilization on N-doped nanocarbon are studied in the direct synthesis of H_2O_2 and compared with undoped catalysts or prepared by the same Pd deposition method on active carbon (Vulcan XC-72). The Pd on N-CNT-like gives high productivities to H_2O_2, comparable to the best literature results. 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. However, the introduction of these N functionalities on the surface has also a negative effect on the rate of H_2O_2 consecutive conversion to water.

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1. Introduction

The direct synthesis of H_2O_2 from H_2/O_2 is increasing of interest with the starting of operations of new large scale processes using H_2O_2 as the oxidant: synthesis of caprolactame and propene oxide [1]. One major problem in the direct synthesis of H_2O_2 derives from the need to operate with diluted H_2 and O_2 gaseous feeds to be outside the explosion range of the O_2/H_2/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 [2–4].

The reaction of direct synthesis of H_2O_2 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 H_2 concentrations (close to lower explosivity limit of the H_2:O_2:inert mixture), still major safety problems remain. In fact, high selectivities in the reaction require to use large O_2 to H_2 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 H_2O_2 with respect to the commercial antraquinone route.

In the past, we explored the possibility of using catalytic membranes/diffusors for intrinsically-safer operations in the direct synthesis of H_2O_2 [5–8]. 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 [9], 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 H_2O_2 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 H_2O_2), (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 [2–4], 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 H_2O_2 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 CO_2 as ballast, because as shown earlier [1,10], the presence of CO_2 modifies the properties of the solvent (methanol) improving in particular the solubilization of oxygen. We refer for this reason as CO_2-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 pyrolitic 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 H_2O_2 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 $55\ m^2\ g^{-1}$ 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 NH_3 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 HNO_3) 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]. Na_2PdCl_4 (0.093 mmol) was dissolved in 100 ml of H_2O, 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 $NaBH_4$ 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, $254\ m^2\ g^{-1}$; 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-Al_2O_3 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 H_2 to H_2O_2 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 CH_3OH as a reaction medium, in order to improve both solubility of H_2 and particularly O_2. Two hundred and fifty microliter of H_2SO_4 were added for H_2O_2 stabilization as reported in previous papers [4,5]. 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 H_2 with a H_2/O_2 ratio of 1:2 and 50% CO_2 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 H_2/O_2 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 H_2 and O_2 was performed using a gas chromatograph unit (Agilent 3000 A equipped with a Molsieve 5 Å column using argon as carrier gas). Conversion of H_2 was calculated by gas analysis before and after reaction. The reaction products were analysed by potentiometric titrations of H_2O_2 (Metrohm, 794 Basic Trino) and H_2O (Metrohm, 831 KF Coulometer), respectively.

Tests in H_2O_2 decomposition were analogous to those of direct synthesis (batch reactor), but introducing already a methanol solution containing a determined amount of H_2O_2 and using a gas feed in which O_2 was substituded with N_2. 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 H_2O_2 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 H_2O_2 formed per mg of Pd (Fig. 1(a) and (b)) as a function of time, or in terms of H_2O_2 concentration (wt%) as a function of time (Fig. 1(c) and (d)).

The results of the tests in batch conditions show total consumption of H_2 after about 1 h and thus all catalysts arrive to a maximum formation of H_2O_2 (in the 1.4–1.8 wt% range). The value depends on the selectivity in H_2O_2 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 H_2O_2 is observed, because the feed of the $H_2/O_2/CO_2$ gas mixture is continuous. In this case a linear increase in H_2O_2 concentration is obtained, with only a slight deviation at the higher H_2O_2 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 H_2O_2 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 CO_2 as ballast, while other results were obtained using N_2 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 terms of type of reaction, and presence of additives, as well as amount of H_2O_2 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 H_2O_2 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 H_2O_2.
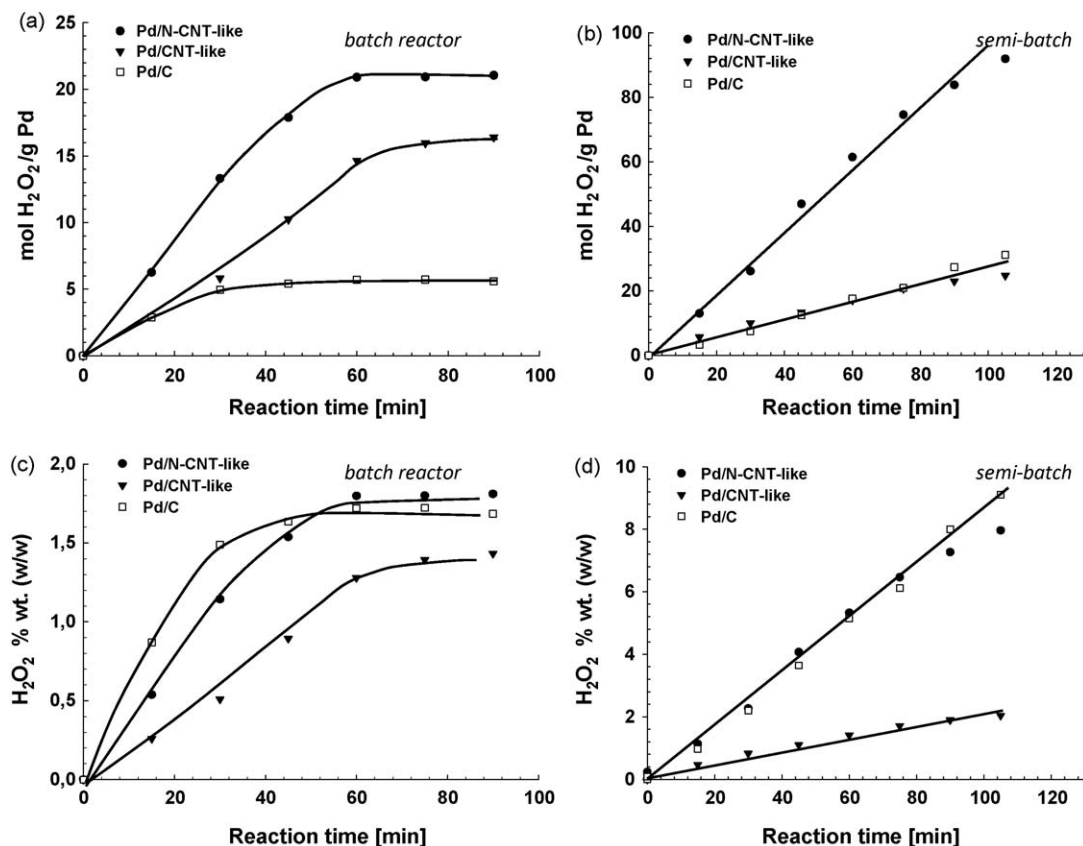

Fig. 1. Catalytic behavior of Pd/CNT-like, Pd/N-CNT-like and Pd/C catalysts in the direct synthesis of H_2O_2 in batch- and semi-batch type reactor. See text for experimental conditions.

Table 1

Catalyst productivity in the direct synthesis of H_2O_2 and comparison with selected literature results.

Catalyst	Mol H_2O_2/(kg$_{cat}$ h)	Selectivity H_2O_2, %	P_{H_2}, MPa	P_{O_2}, 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 CO_2 as ballast on the catalyst activity and selectivity in H_2O_2 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_2O_2/g Pd h	1.18	0.35	1.59	0.41
Selectivity H_2O_2, %	30	10	39	11

Reported in Table 2 is the effect of the total pressure and use of CO_2 or N_2 as the ballast in the direct synthesis of H_2O_2, 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 H_2O_2 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 CO_2 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 CO_2 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 CO_2.

The effect of CO_2 was also observed in other reactions of oxidation such as the p-xylene oxidation to terephthalic acid and interpreted as equilibrium between CO_2 and peroxocarbonate species which enhances the amount of solubilized oxygen in methanol [1,15]. Increasing the oxygen partial pressure it is thus reasonable to obtain higher selectivities to H_2O_2. 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 H_2O_2.

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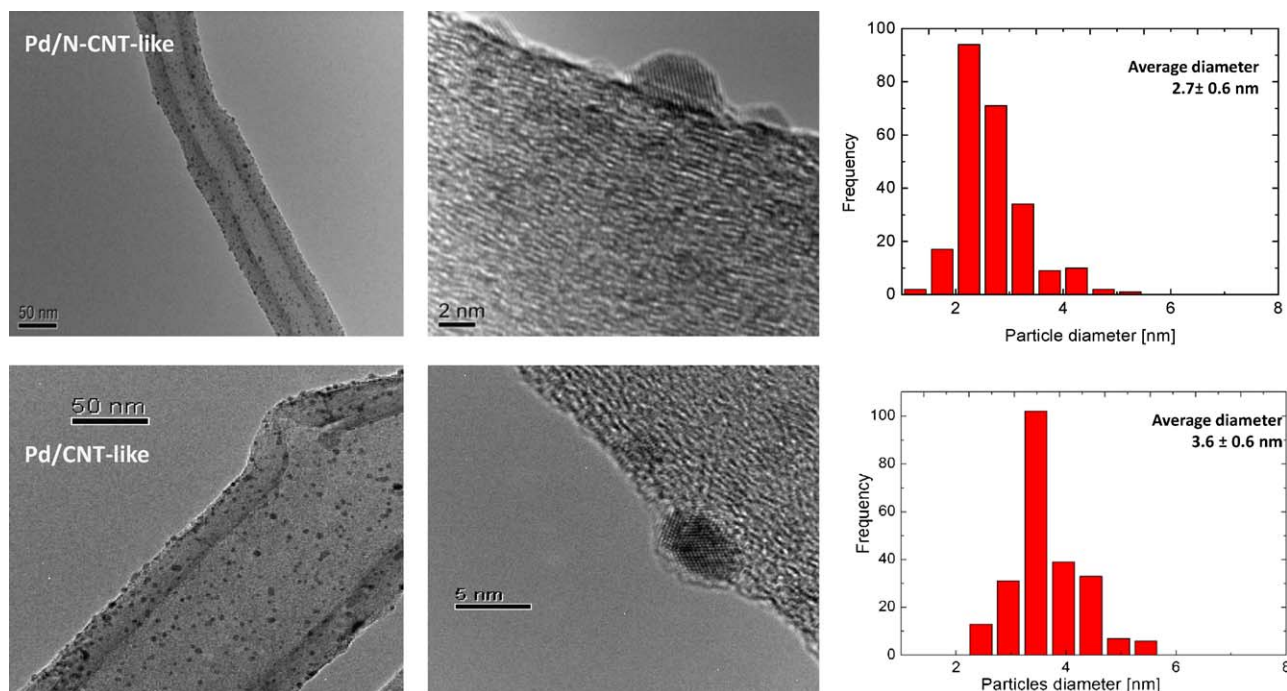
Fig. 2. HRTEM images of Pd/N-CNT-like and Pd/CNT-like samples, and relative distribution of Pd particles.

Table 3

Surface area and mean diameter of Pd nanoparticles (estimated from HRTEM data) and specific rate of H_2O_2 formation per m^2 of Pd surface area in the studied catalysts.

	Pd, wt%	Average diameter Pd particles, nm	Surface area Pd particles		mol H_2O_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

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 H_2O_2 per m^2 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 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 O_2 surface coverage and the rate of H_2O_2 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 H_2O_2 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 H_2O_2 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.

As described in Section 2, these tests were similar to those of H_2O_2 synthesis, except that oxygen is substituted with nitrogen, and hydrogen peroxide is already present at the start of the
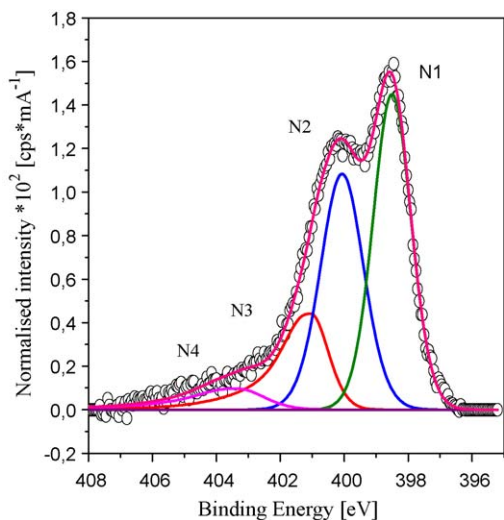
Fig. 3. XPS spectrum (synchrotron radiation) in the N 1s core level region of N-CNT-like sample. See text for spectral deconvolution.
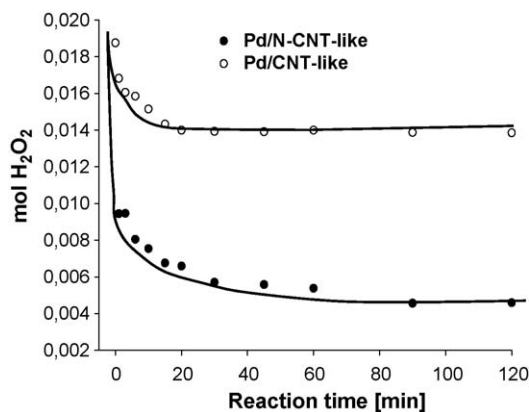
Fig. 4. Tests of H_2O_2 hydrogenolysis and decomposition on Pd/CNT-like and Pd/N-CNT-like samples.

reaction. In these tests it is thus possible to evaluate the combined rate of hydrogenolysis and decomposition of H$_2$O$_2$. 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 H$_2$O$_2$. As noted earlier [1,4], the H$_2$O$_2$ hydrogenolysis is one of the main pathways responsible of selectivity lowering in the synthesis of H$_2$O$_2$ and it is thus necessary to make tests in the presence of H$_2$ to obtain indications on the relative relevance of consecutive reactions of H$_2$O$_2$ conversion to water in the different catalysts.

The results reported in Fig. 4 clearly evidence that the rate of H$_2$O$_2$ 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 H$_2$O$_2$ 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 improves the selectivity. However, further studies are necessary to better understand this question.

4. Conclusion

CNT-like materials as well as graphitic-type carbon show excellent properties as support for Pd nanoparticles to prepare catalysts for the direct synthesis of H$_2$O$_2$. The potential advantages of CNT-like materials for their use in microchanneled reactors were also highlighted. The introduction of N functionalities in CNT-like materials, by treatment with ammonia at 873 K after oxidizing pretreatment, further enhances the productivity

and turnover (specific activity per m^2 of surface area of Pd) of the catalyst. The effect is possibly related to the electronic effect of pyridine-like nitrogen sites present in the N-CNT-like support in favoring the O$_2$ surface coverage on Pd nanoparticles. However, the introduction of these N functionalities on the surface has also a negative effect on the rate of H$_2$O$_2$ consecutive conversion to water.

References

[1] G. Centi, S. Perathoner, Catal. Today 143 (2009) 145.
[2] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem. Int. Ed. 45 (2006) 6962.
[3] C. Samanta, Appl. Catal. A: Gen. 350 (2008) 133.
[4] G. Centi, S. Perathoner, A. Abate, Modern Heterogeneous Oxidation Catalysis, N. Mizuno (Ed.), PN Wiley-VCH Pub., Weinheim, Germany, (2009) p. 253, Chapter 8.
[5] S. Abate, S. Melada, G. Centi, S. Perathoner, F. Pinna, G. Strukul, Catal. Today 117 (2006) 193.
[6] S. Abate, G. Centi, S. Perathoner, S. Melada, F. Pinna, G. Strukul, Top. Catal. 38 (2006) 181.
[7] S. Melada, F. Pinna, G. Strukul, S. Perathoner, G. Centi, J. Catal. 237 (2006) 213.
[8] S. Melada, F. Pinna, G. Strukul, S. Perathoner, G. Centi, J. Catal. 235 (2005) 241.
[9] A.L. Tonkovich, K.T.P. Jarosch, D.J. Hesse, US Patent 7,029,647 (2006), assigned to Velocys (US).
[10] S. Abate, K. Barbera, P. Lanzafame, S. Perathoner, G. Centi, Preprints—Am. Chem. Soc., Div. Petrol. Chem. 53 (1) (2008) 227.
[11] J.P. Tessonier, D. Rosenthal, T.W. Hansen, C. Hess, M.E. Schuster, R. Blume, F. Girgsdies, N. Pfänder, O. Timpe, D. Su, R. Schlögl, Carbon 47 (2009) 1779.
[12] R. Arrigo, M. Hävecker, R. Schlögl, D.S. Su, Chem. Commun. 40 (2008) 4891.
[13] A. Villa, N. Di Wang, F. Porta, D. Su, L. Prati, J. Catal. 244 (2006) 113.
[14] J.K. Edwards, B. Solsona, E. Ntainjua N, A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Science 320 (2009) 20.
[15] G. Centi, S. Perathoner, Catal. Today (2009), doi:10.1016/j.cattod.2009.07.075.
[16] N. Dimitratos, J.A. Lopez-Sanchez, D. Morgan, A. Carley, L. Prati, G.J. Hutchings, Catal. Today 122 (2007) 317.
[17] G.B. Brieva, E.C. Serrano, J.M.C. Martin, J.L.G. Fierro, Chem. Commun (2004) 1184.
[18] B. Zhou, K.-K. Lee, US Patent 6,168,775 (2001), assigned to HTI.
[19] T. Haas, G. Stochniol, J. Rollmann, US Patent 7005528 (2006), assigned to Degussa AG (Germany).
[20] G. Paparatto, R. D'Alosio, G. de Alberti, R. Buzzoni, US Patent 7,122,501 (2006), assigned to Eni/EniChem.