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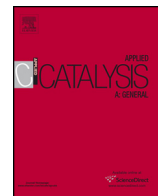
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Pd nanoparticles prepared by grafting of Pd complexes on phenol-functionalized carbon supports for liquid phase catalytic applications



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ABSTRACT

An activated carbon was functionalized by oxidation with HNO₃ or H₂O₂ to increase the number of acidic groups on its surface. A sample of HNO₃-oxidized carbon was treated thermally to remove unstable functions. Detailed characterization by a combination of techniques revealed that this stabilization procedure allowed selecting weaker acid sites of phenolic type. H₂O₂ functionalization gave also mainly surface phenols but in lower amounts. Palladium grafting was carried out in water at room temperature by ligand exchange between a carboxylate complex and the surface oxygenated groups. Activation was carried out thermally and the samples grafted on the most oxidized supports proved more difficult to reduce. The catalytic activity of the obtained Pd/C catalysts was evaluated in the reduction of 2-methyl-2-nitropropane (MNP) into *t*-butylamine (TBA). The most active materials were those prepared on H₂O₂-modified carbon and on the stabilized support. In the latter case, the superior activity was explained by the robustness of the grafting anchors which could not decompose during thermal activation together with the active role of weak acidic groups in the catalytic reaction itself.

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1. Introduction

Among industrially relevant supports for heterogeneous catalysts, activated carbon is a judicious choice because of several interesting characteristics [1,2]. It is relatively inert and stable mechanically, presents a high surface area and allows recovery of the metal content by calcination. Moreover, it is widely available in various forms at limited cost. Carbon-supported catalysts are usually prepared by deposition or impregnation. However, recent research efforts are directed toward more rational preparation procedures [3]. In this respect, we aim at using covalent grafting to introduce the metal complex on the carbonaceous surface to control its distribution on the support.

Activated carbons present naturally a range of surface chemical functions, mainly oxygenated. These originate in the raw materials or are introduced during the activation step. The oxygen content may vary from 1 to 25% depending on the source and activation procedure [4]. The other constituents, apart from C and H, are usually N and S together with some inorganic oxides (ashes). The hetero-atoms are present as surface functional groups and confer acido-basic properties to the material. The oxygen-containing

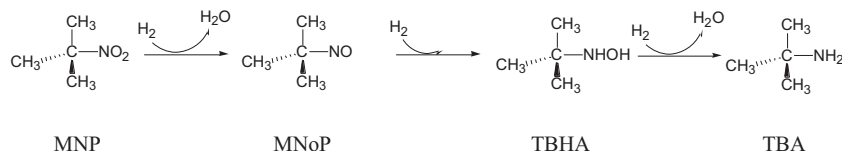
acidic groups are usually identified as carboxyl, lactones, phenols and lactol groups, while basicity is probably carried by chromenes, ketones or pyrones [5]. The nature and amount of each function can be assessed by so-called Boehm titrations [6,7]. Instrumental techniques such as TPD, XPS or infrared spectroscopy complement those titrations [8].

The number of surface oxygenated groups can be increased by oxidation. This is carried out in gas phase with air [9], oxygen [10], ozone [11], or in the liquid phase with nitric acid, H₂O₂, sodium persulfate, potassium dichromate, etc. [12]. The experimental variables have a profound influence on the results obtained in terms of nature as well as quantities of functions introduced. Oxidative functionalization will change the hydrophilicity of the carbon materials, its surface charge and textural properties with consequences on behavior in various applications [13]. Properties can thus be adjusted to needs. In addition, surface groups can be decomposed by thermal treatment under inert atmosphere [14].

Grafting preparation methods have been widely used for inorganic oxides as catalytic supports, such as silica, which are rich in surface hydroxyls that react easily with a range of organometallic molecules. Grafting on carbonaceous supports is less frequently encountered because less surface functions are available naturally. The group of Freire et al. has immobilized metal complexes of Cu, Mn or Ni via the ligands, using surface oxygenated groups as anchors [9,15–17]. Acetylacetonate complexes have also been covalently anchored onto functionalized carbons via diamine

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Scheme 1. Reduction of 2-methyl-2-nitropropane (MNP) into *t*-butylamine (TBA).

linkers [18]. Direct C–O–M bonds are scarcely reported. It was postulated for Rh without direct evidence [19].

Correlations between the number of oxygenated surface groups and catalytic activity have been established very early [20]. Preoxidation of polymer-derived carbons lowered catalyst activity whereas preoxidation of a carbon black composite support increased it. Similar mixed results have been reported in the literature since. Then, a correlation was found between the amount of O-groups and the metallic dispersion in the final catalyst [21]. This can be interpreted as a decrease of carbon hydrophobicity by functionalization which is favorable for wettability during the impregnation step. The interactions between metallic precursors and the various surface sites have been studied and one report claims that it is the phenols that allow the strongest interactions [22]. Functionalization also affects textural characteristics such as surface area or pore sizes [23]. These might influence metal dispersion and catalytic activity. During activation, especially if carried out thermally, the most fragile functions can decompose. If the metallic precursors were in interactions with those, important sintering can take place [24].

The goal of the present study is to prepare Pd/C catalysts by covalent grafting of metallic precursors. By covalent grafting, we mean chemical bond between metallic precursor and carbon support. This study provides insight on (i) the possibility to form such a bond and prove its existence and (ii) its advantage or inconvenience for the catalytic activity of the final Pd/C material arising from it. Indeed, in the literature, grafting is very often presented as a catalyst synthesis technique, with no detailed characterization of the grafted fragment before reduction/activation. However, the activated catalyst retains the memory of the precursor stage.

The aim here is to use experimental conditions in which grafting indeed occurs and to connect activity with initial characteristics of the material. Grafting is generally believed by many authors to lead to increased metal dispersion in the final catalyst, but other more subtle effects might take place due to the specific conditions (for instance support functionalization, specific type of solvent, choice of metallic precursor, etc.) that are required during synthesis.

In our case, the carbon support was functionalized by oxidation to create oxygen-containing surface groups that might act as anchors for metal precursors. The Pd precursor was selected among Pd carboxylate complexes to allow ligand exchange with surface oxygenated groups. If such a ligand exchange does occur, the Pd^{II} metal center becomes bonded covalently to the surface through a new Pd–O bond. Knowing that the goal is to exchange one carboxylate (anionic) ligand in the precursor complex against one surface function (anionic), we consider that only carboxylic acids and phenols on the surface might act as surface ligands after deprotonation. At the end of the contact period, the solid is filtered out and abundantly washed to remove any metal species non-covalently bound on the surface. The feasibility of this strategy has already been demonstrated [25]. Here, we will stabilize the functionalized supports by removing the most fragile functions. This is important to ensure absence of sintering during activation by thermal heating. The functionalized and stabilized supports, as well as grafted complexes, need thus to be characterized in detail to get a precise picture of surface species at each step of the preparation procedure and after activation. Activation by heating will result in

reduction of Pd^{II} into Pd⁰ and removal of remaining ligands of the starting complex. This causes the Pd atoms to coalesce into metallic nanoparticles.

The reaction studied with the obtained carbon-supported Pd nanoparticles catalysts is the reduction of 2-methyl-2-nitropropane (MNP) in *t*-butylamine (TBA) (Scheme 1). Aliphatic amines present an interest for pharmaceutical and photographic industries, as well as for rubber production [26].

2. Experimental

2.1. Support functionalization

The selected activated carbon SXplus (noted SX+, $S_{\text{BET}} = 922 \text{ m}^2/\text{g}$) from NORIT was sieved to keep only particles with diameter in the range 50–100 μm .

It was functionalized by reaction with HNO_3 as follows. In a three-necked round bottom flask, typically 2 g carbon powder are suspended in 50 mL nitric acid and stirred for 24 h. We have upscaled this to 4 or 6 g carbon in 100 or 150 mL nitric acid, respectively, without any problem of reproducibility. Two parameters were modified: nitric acid concentration and temperature. A reflux condenser was added above the flask when working under refluxing conditions, fitted with a trap for acidic vapors which was filled with a base in aqueous solution. After reaction, the carbon was filtered out, abundantly washed with distilled water, then washed with water on a Soxhlet apparatus for 24 h, and finally dried at 50 °C for 4 h minimum under vacuum.

The SX+ carbon was treated by H_2O_2 11.7 mol L^{-1} (Acros) by suspending 4 g carbon in 100 mL H_2O_2 at room temperature. The carbon was filtered out, abundantly washed with distilled water, then on a Soxhlet apparatus for 24 h before being dried at 50 °C under vacuum.

Stabilized supports were obtained by heating the powders in a tubular oven at 500 °C for 8 h under nitrogen flux. The heating and cooling ramps were fixed at 100 °C/h. Mass losses during stabilization were determined by comparing the mass after heating at 110 °C overnight with the final mass obtained after stabilization at 500 °C.

The functionalized supports will be noted **R** when treated under reflux, **A** when using room temperature, **S** when stabilized, and the oxidant concentration is specified besides its nature.

2.2. PZC and Boehm titrations

The point of zero charge (PZC) has been determined following a literature method [27,28]. 1 g carbon was suspended in 10 mL water at fixed pH value. After 24 h stirring, the final pH is measured. When plotting the final pH versus initial pH, the curve gives a plateau that is the PZC value.

Solutions of NaOH and Na_2CO_3 were prepared by dilution of commercial standards (Fixanal from Riedel-de-Haën and Titrisol from Merck, respectively). The NaHCO_3 solution was prepared by dissolution of 4.213 g of solid NaHCO_3 (Fluka) in 1 L distilled water in a volumetric flask (to obtain a $\sim 0.05 \text{ mol L}^{-1}$ solution) followed by titration with NaOH solution to determine the exact concentration. The HCl solutions were prepared from 37% concentrated

reactant (VWR) and titrated with NaOH. All solutions were prepared with decarbonated water (freshly distilled and flushed with nitrogen) and kept under nitrogen.

To titrate the acidic functions, 0.5 g carbon were suspended in 50 mL base (NaHCO_3 0.05 mol L⁻¹, Na_2CO_3 0.025 mol L⁻¹ or NaOH 0.05 mol L⁻¹). After 24 h stirring, the carbon is filtered out and aliquots are titrated rapidly by HCl 0.025 mol L⁻¹. The indicators were phenolphthalein for NaOH and bromothymol blue (upon boiling) in the cases of NaHCO_3 and Na_2CO_3 .

The basic functions were titrated by suspending 0.5 g carbon in 50 mL HCl 0.05 mol L⁻¹. After 24 h stirring, the filtrate is titrated with NaOH 0.025 mol L⁻¹ with phenolphthalein as indicator.

2.3. Synthesis of Pd precursor

The $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ complex was synthesized following a procedure from the literature [29]. Yield: 81%; IR: $\nu(\text{COO})_{\text{sym}}$. 1374 cm⁻¹, $\nu(\text{COO})_{\text{asym}}$. 1599 cm⁻¹; EA: Exp. C 38.89, H 7.69, N 7.52%, Calc. C 38.87, H 7.61, N 7.56%; TGA: Exp. 70%, Calc. 71% (Pd residue).

2.4. Grafting of Pd precursor on functionalized SX+ carbon

The amount of Pd introduced in solution corresponds to a theoretical 5 wt.% loading in the final catalyst which was verified by atomic absorption analysis of the grafting filtrates at the end of the procedure. In a typical experiment, 0.17 g $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ complex are dissolved in 50 mL distilled water. This solution is added to 0.95 g carbon powder (functionalized or not). After 24 h stirring at room temperature, the solid sample is recuperated by filtration, washed with distilled water and dried at 50 °C under vacuum. The filtrates with the washings are poured in a 100 mL volumetric flask.

2.5. Thermal activation to form supported nanoparticles from the Pd grafted samples

The catalysts were activated in order to remove the ligands and reduce Pd^{II} into Pd⁰ to produce supported Pd nanoparticles as active phase by heating in a Carbolite tubular oven (type STF 16/450) under nitrogen flow at 200 °C for 4 h. The samples were contained as thin layers in porcelain combustion boats.

2.6. Catalytic tests

The catalytic tests for 2-methyl-2-nitropropane (MNP) hydrogenation into *t*-butylamine (TBA) (Scheme 1) were carried out in a steel Parr 4521 reactor fitted with a temperature control device and a mechanical stirrer fixed at 2500 rpm. In these conditions, extra-granular diffusion limitations are avoided and kinetic regime is guaranteed [30]. 350 mL methanol (Fluka, p.a. >99.8%), a known quantity (about 0.3 g) of catalyst and 3 mL 1-propanol (chromatographic internal standard, Acros, p.a. 99+%) were poured in the reactor and degassed (15 min) under nitrogen. A pretreatment was applied to the catalyst at 80 °C for 1 h, under 17 bar of H₂ to clean the surface that might have been passivated by handling under air after activation and avoid consumption of hydrogen by the catalyst itself during the first stages of catalysis. The reactant (MNP, Alfa Aesar, 99%) was dissolved in 25 mL methanol and degassed (under N₂) before being added in the reactor via a pressurized addition ampoule together with a last portion of 25 mL degassed methanol without opening the reactor to the air. The initial reactant concentration is thus 0.1515 mol L⁻¹. During catalytic reaction, the reactor was kept under a pressure of about 12 bar H₂ and a temperature of 60 °C. Aliquots of the reaction mixture are taken at regular time intervals and analyzed by gas chromatography (GC). Further details

are provided elsewhere [30]. At the end of the test, the catalyst is separated from the reaction mixture by filtration.

The GC chromatograph was an Agilent Technologies 6890 N fitted with a WCOT fused silica Chrompack CP-WAX 52 CB capillary column (*l* = 50 m, internal diameter = 0.53 mm, thickness of the film = 2 μm). The vector gas was He (50 kPa) and the temperature of the injector and detector was kept at 250 °C. The samples were automatically injected via a split-splitless injector with a split flow of 20 mL min⁻¹. The temperature program for analysis was as follows: 160 °C for 5 min, heating to 240 °C (10 °C min⁻¹), isotherm at 240 °C for 2 min. The signal received by a FID detector was directly interpreted by a computer using the HP Chemstation software. The area of each peak was converted into concentration by applying the response factor with respect to the internal standard.

The specific activity measured can be expressed either by the conversion rate of MNP or by the rate of formation of TBA. In this study, the catalysts are compared on the basis of the former, because an apparent zero-order is always observed, hence the slope of the curve MNP consumption versus time is proportional to the catalyst amount. The presented results are normalized with respect to the mass of catalyst used. The catalytic activity evaluated from the MNP consumption rate is expressed in mmol min⁻¹ g⁻¹. Some TBHA intermediate was detected but always in very small amounts, and with no variation from one catalyst to the other. The 2-methyl-2-nitrosopropane (MNoP) intermediate does not accumulate in the reaction medium: it is known to be very reactive [31].

2.7. Instrumental

Infrared (IR) spectra of functionalized carbon samples were recorded on a FT-IR Bruker Equinox 55 spectrophotometer in absorbance mode from KBr disks prepared from 500 mg KBr for 1 mg carbon sample and dried overnight at 110 °C. For metallic complexes, spectra were recorded in transmittance, using KBr disks containing 1 wt.% sample.

Thermogravimetric analyses (TGA) were carried out on a TGA/DSC combined SDTA 851e apparatus from Mettler-Toledo. The samples (~5 mg) were placed in 70 μL alumina containers, and submitted to a 10 °C min⁻¹ heating ramp under 100 mL min⁻¹ nitrogen flow.

The amounts of metal present in solution were determined by atomic absorption (AA) on a Perkin-Elmer 3110 spectrometer equipped with a flame atomizer. Calibration curves were established with Pd standard solutions of concentration 1–10 mg L⁻¹.

C–H–N elemental analyses (EA) were carried out by the microanalysis service of University College London, UK.

The metal loading in solids was determined, after digestion overnight in a mixture of strong acids, by ICP-OES, by the Medac Ltd. Company (UK). Oxygen content (direct measure, not difference) was also determined by Medac on a Thermo FlashEA1112 elemental analyzer, after pyrolysis of the sample under catalytic conditions that produces oxygen bound as carbon monoxide.

X-ray Photoelectron Spectroscopy (XPS) was carried out at room temperature on a SSI-X-probe (SSX-100/206) spectrometer from Fisons connected to a computer running the S-probe software. The samples were fixed by double-face isolating sticky tape on small brass troughs and placed on a ceramic rotating sample holder (Macor®, Switzerland), capped by a Ni grid on a 3 mm O-ring to avoid charge effects. The absence of signal arising from underlying sticky tape was verified. During analysis, the created surface charges were neutralized by a floodgun of energy fixed at 8 eV. The pressure in the analysis compartment was 10⁻⁶ Pa. The data were interpreted with the CasaXPS software. The photopeaks were calibrated with reference to the C–C_{1s} component which was fixed at 284.8 eV. The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction

of a Shirley baseline. Constraints were used for decomposing the Pd3d peak: area ratio (Pd3d5/2/Pd3d3/2 = 1.5, difference in energy Pd3d3/2 – Pd3d5/2 = 5.26, FWHM = 1. A first doublet appears at Pd3d5/2 = 335 eV (Pd⁰), while the second is 3 eV further for Pd^{II}. The C1s envelope of functionalized carbons has been decomposed by imposing always the same number of sub-components with identical FWHM between 292.6 and 281.0 eV.

X-ray powder diffraction (XRD) analyses were carried out on a SIEMENS D5000 diffractometer equipped with a copper anticathode ($\lambda_{\text{CuK}\alpha}$ = 154.18 pm). The samples were supported on quartz monocrystals. The detected phases were identified by reference to the JCPDS database.

The nitrogen adsorption–desorption isotherms were recorded on an ASAP 2000 or ASAP2020 instrument from MICROMERITICS at 77 K. The sample (0.1 g) was degassed under 4 μmHg pressure for several hours at 200 °C before the analysis. The specific surface area was calculated from the adsorption data using the Brunauer–Emmett–Teller (BET) method even though it is not ideal for microporous solids but it allows making comparisons between similar samples.

Metallic dispersion measurements were conducted by CO chemisorption with a PULSE CHEMISORB 2700 apparatus from Micromeritics. The sample (about 30 mg) was first reduced under a hydrogen flow (30 mL min^{−1}) at 150 °C during 1 h. Then, it was swept by a helium flow (30 mL min^{−1}) at 200 °C for 2 h. The sample was finally brought back to room temperature at which it was subjected to a sequence of CO pulses. The metallic dispersion was calculated from the cumulative amount of adsorbed CO (i.e. the sum of non-detected CO in each pulse), following:

$$D = \frac{V_{\text{NTP}} \cdot M}{V_M \cdot m \cdot C \cdot P} \times 100$$

where D is the metallic dispersion (%), V_{NTP} is the adsorbed volume under normal temperature and pressure conditions, M is the atomic weight of the metal (here, Pd), V_M is the molar volume (22.414 L mol^{−1}) of the active gas at normal conditions (0 °C, 1 atm), m is the dry sample mass, C is the stoichiometric coefficient for CO adsorption on Pd (a 1:1 stoichiometry was used in the present study as it is regularly done within the framework of comparisons between similar samples [32–34]) and P is the wt.% of metal in the sample. The amount of Pd taken into consideration for the calculations was the proportion of Pd⁰ determined by XPS in the activated samples, to avoid artifacts due to difficulties in reducing the grafted samples within the CO chemisorption apparatus.

The Scanning Electronic Microscopy (SEM) images were obtained on a FEG Digital Scanning Microscope (DSM 982 Gemini from LEO), equipped with an EDAX detector (Phoenix CDU LEAP). The samples were fixed by double-face conductive carbon sticky tape on 5 mm diameter Al specimen stubs (Agar Scientific).

Transmission Electronic Microscopy (TEM) images were obtained on a LEO 922 OMEGA Energy Filter Transmission Electron Microscope operating at 200 kV. The solid samples were suspended in hexane or ether under ultrasounds. One drop of supernatant containing the smallest particles was then deposited on a holey carbon film supported on a copper grid, before being dried at room temperature overnight under vacuum.

3. Results and discussion

3.1. Carbon support functionalization

The SXplus (noted SX+) carbon support was functionalized by treatment in the liquid phase either with HNO₃ at room or refluxing temperature during 24 h or with H₂O₂ at room temperature for variable durations. This is redundant with respect to our preliminary study [25], but these functionalized supports have been

more extensively characterized here. In particular, the quantification of each different type of oxygen functionalities was sought. In addition, for some highly functionalized supports, the most fragile functions were removed by stabilization at 500 °C under inert atmosphere (before any contact with Pd precursor). The starting support contains 6 wt.% oxygen, which increases significantly upon oxidation (see Table S1 in Supporting Information (SI)). The increase is much more pronounced (Table S1, O wt.%) for HNO₃ (up to 300%) than H₂O₂ (~30%) and heating at 500 °C indeed causes a 50% drop in the oxygen content. When measuring the point of zero charge [27] of the different carbon samples obtained, we observed a marked decrease when functionalizing with HNO₃, a slight decrease with H₂O₂, and a backwards shift to higher value when stabilizing (Table 1).

The functionalized supports were characterized by Boehm titrations [35,36]. This is a standard procedure to characterize oxygen-containing groups in carbon samples, and had already been carried out to determine the so-called 'total' acidity on samples prepared similarly in our exploratory undertakings [25]. Here, we will go further and use different bases to titrate different acidic surface groups, but also titrate the surface basic groups (see below). As both catalyst preparation and catalytic reaction will be carried out in liquid phase, a titration procedure carried out in water is more pertinent that measurement made on the solid in the gas phase. As shown before, the 'total' number of acidic functions (Table 1) increases after oxidation, and more in the case of HNO₃ than H₂O₂. There is a clear correlation between PZC and 'total' acidity values. The nitric acid concentration and temperature of treatment had a marked effect, as already reported [37,38]. In the case of H₂O₂, these parameters had a less noticeable influence. If the functionalized samples are water-washed in a Soxhlet apparatus for long periods of time (we tested up to one week), and titrated again, the figures obtained are the same. This shows that the carbon materials acidity is not only due to the presence of acids reactants adsorbed on the surface that could have been washed out. The acidity cannot be removed proving that the oxidant did chemically react with the carbon support. The starting carbon presents nearly as much basic than acidic sites, but these decrease when functionalizing with HNO₃ (Table 1), and increase slightly in the case of H₂O₂.

The functionalized carbons were also characterized by XPS. O/C ratios followed the trends observed via Boehm titrations and increased more with HNO₃ than H₂O₂ treatment, as well as decreased upon heating in inert atmosphere. A linear correlation appeared between total acidity and O/C values from XPS, as reported previously [25]. However, the line does not comprise the origin (Fig. S1 in SI). If going further and plotting XPS values against the sum of acid and basic sites titrated, then it includes the origin (Fig. 1). This means that (i) all functions are indeed titrated and (ii) the surface is not very different from the bulk, i.e. the functionalization occurs in a homogeneous fashion. The only sample standing out of the general trend is the stabilized carbon, where some basic groups containing no oxygen must have been created by heating. These are probably electron-rich sites [6]. The correlation between XPS and bulk elemental analyses results is also rather good, except for the most functionalized samples, where the surface presents a lower amount of oxygen than the bulk. So there is a contradiction (for those exceptions only) with the above statement on the correlation between Boehm titration and XPS, and this should be related to textural damage. Indeed, the fact that some pores were widened and/or opened by the harsh treatment gives more easy access to the internal surface in these cases.

Boehm titration with different bases allows distinguishing between carboxylic acids, lactones and phenols (Fig. 2). The non-treated carbon already presented the three types of acid groups. With HNO₃ oxidation the carboxylic acids increased strongly. Phenols also increased, but lactones first increased slightly with mild

Table 1

Results of total acid and basic Boehm titrations (average values for many different samples), N/C surface ratios determination, point of zero-charge (PZC), specific surface area and density of acid functions.

Functionalization ^a	PZC	Acidity (mmol/100 g _c)	Basicity (mmol/100 g _c)	N/C (× 100) from XPS	S _{BET} (m ² /g)	Density of acid functions (mmol/100 nm ²)
None (SX+)	8.1	28	25	0.33	922	18
0.2HNO ₃ -A	4.1	57	21	0.33	916	37
0.2HNO ₃ -R	3.1	116	16	0.89	913	76
1.0HNO ₃ -R	2.4	218	13	1.12	793	165
2.5HNO ₃ -R	2.1	311	2	1.50	756	248
2.5HNO ₃ -R-S	6.0	126	105	1.20	720	86
11.7H ₂ O ₂	5.1	62	32	0.37	1000	37

^a The functionalized supports are noted **R** when treated under reflux, **A** when using room temperature, **S** when stabilized, and the oxidant concentration (in mol L⁻¹) is specified besides its nature.

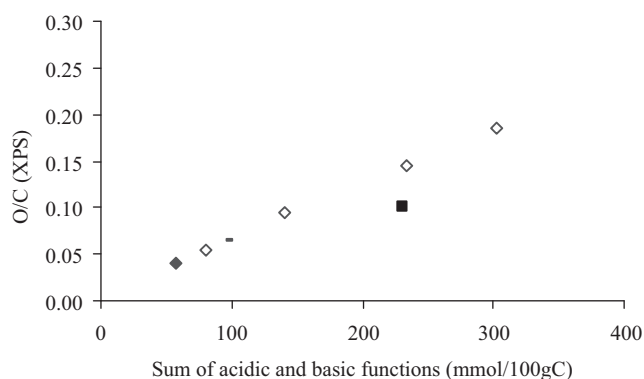


Fig. 1. Correlation between O/C ratios (XPS) and sum of acidity and basicity (Boehm titrations): (◆) unmodified SX+, (◇) SX+ functionalized with HNO₃, (○) SX+ functionalized with H₂O₂, (■) stabilized SX+.

treatments, then decreased when using concentrated acid due to opening of their ring structures. These results are in agreement with previous reports [39]. In the case of H₂O₂, phenols are the most significant functions, followed by carboxylic acids (Fig. 2). In conclusion, the two oxidative reactants do not create oxygenated groups of same nature, as already reported in the literature since many years [21,44].

When removing the most fragile functions by heating, the total acidity measured by Boehm titration decreases drastically (Table S2a in SI) while the basicity increases (Table 1). In parallel, the PZC value shifts back toward the value of starting SX+ without reaching it, and without coinciding with the PZC value of 0.2HNO₃-R sample of similar total acidity prepared in diluted nitric acid. This is due to the presence of more basic sites. The acidity decrease is due to decomposition of carboxylic acid groups (as CO₂), and partial degradation of phenols (Table S2b in SI). This effect is also known

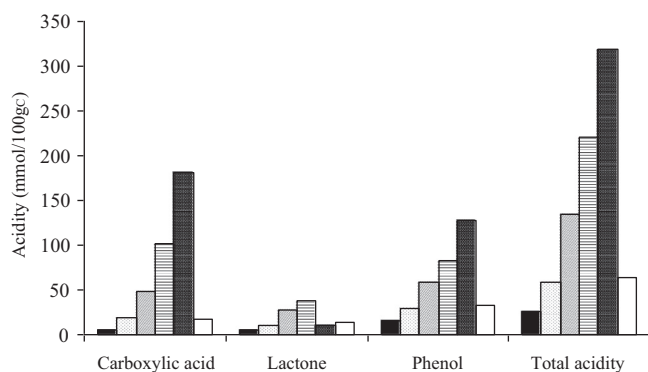


Fig. 2. Acidic groups determined by Boehm titrations for functionalized carbon samples: ■ non-functionalized SX+, □ 0.2HNO₃-A, ▨ 0.2HNO₃-R, ▩ 1.0HNO₃-R, ■ 2.5HNO₃-R and □ 11.7-H₂O₂.

since a long time [14,40]. Lactones by opposition increase, due to ring closure upon thermal treatment by condensation of one carboxyl with one phenol group [40]. This means that 0.2HNO₃-R and stabilized samples, even though presenting the same total acidity, do not present the same types of acidic and basic functions at their surfaces. When repeating the same thermal treatment again on the same sample, the acidity remains stable, showing that the remaining functions are indeed thermally stable.

It is also possible to distinguish the different oxygenated functions by decomposing the C1s or O1s XPS photopeaks. Given the smaller shifts of oxygen components (Table S3a) [6,40] and interference with water at 535 eV, we have based this analysis on carbon. Knowing that graphitic carbon gives rise to asymmetric C1s peaks, we postulate that the aliphatic/aromatic ratio does not change during functionalization, and used the results in a comparative manner amongst our different samples arising from the same starting solid. As a compromise with regard to varying values in the literature (see Table S3b in SI), we considered five components (Fig. 3). The detailed numbers obtained are given in SI (Table S3c) and confirm that HNO₃ oxidation increases phenols and carboxyls, while H₂O₂ increases all types. The carboxylic acid groups are the most

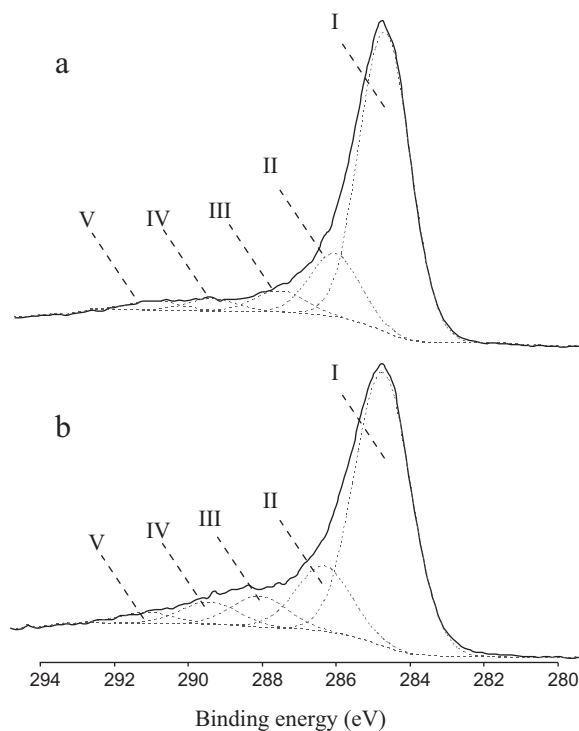


Fig. 3. Decomposition of C1s photopeak for (a) unmodified SX+ and (b) 2.5HNO₃-R: (I) C–C,H of graphitic carbon, (II) C–O of phenols and ethers, (III) C=O of carbonyls and quinones, (IV) carboxyls and esters and (V) π electrons.

fragile because they diminish drastically with stabilization at 500 °C. This is in agreement with Boehm titrations. Carbon atoms connected to nitrogen (C–N) are indiscernible from C–O and might also contribute to the C1s envelope. Indeed, nitrogen is present at the surface in small amounts in SX+ carbon and when functionalizing with H₂O₂, but increases significantly when using HNO₃ (see Table 1). The main contribution to this increase is detected as a new component at 406 eV within the N1s photopeak, attributed to –NO₂ (nitro) groups. These are formed via nitronium ions attack arising from nitric acid and are more numerous when strengthening the functionalization conditions, but diminish during stabilization. These nitro groups could not be observed by infrared spectroscopy (Fig. S2) but IR spectra of the different functionalized samples showed increases of bands at 1700 cm^{–1} (C=O of carboxyls and lactones), 1600 cm^{–1} (C=O, C=C) and 1200 cm^{–1} (C–O) in agreement with results of other techniques discussed above and the literature [40].

The starting SX+ is mainly microporous but also contains some mesopores. The textural characteristics are not strongly modified by functionalization or any subsequent treatment (see Section S0 in SI). The harshest conditions lead to a slight decrease in surface area, with less micropores and more mesopores, showing that it is the limit not to alter the material itself by the oxidation procedure. As stated before [25], the specific surface area S_{BET} decreases slightly when treating with concentrated nitric acid, and increases with H₂O₂ (Table 1). This is due to decrease of micropore volume and pore blocking in the first case, and to mesopore widening in the second case. These different behaviors can be explained by the ability of nitric acid to damage the carbon structure and liberate polyaromatic highly functionalized fragments that become soluble hence highly mobile. These fragments can block the smallest pores. Hydrogen peroxide being a softer oxidant might wash away some impurities but leads to less carbon skeleton dissolution. The stabilized 2.5HNO₃-R-S support presents similar surface than 2.5HNO₃-R after heating i.e. lower than starting SX+, meaning that it has been damaged beyond repair by functionalization. Nevertheless, the final surface area remains high (720 m²/g). We have calculated a density of acidic groups (Table 1), which varies between 18 and 248 acidic functions per 100 nm². We have thus obtained from the same starting carbon very different supports, which will be used for Pd grafting.

3.2. Palladium grafting

The [Pd(OAc)₂(Et₂NH)₂] complex has been selected for incorporation on functionalized carbons by grafting because it is soluble in water and undergoes easily ligand exchange reactions. We postulate that if undergoing ligand exchange for surface oxygenated groups, it will be grafted covalently. This was demonstrated by using model-compounds and fluorinated carboxylates in our previous study [25]. When suspending the various supports in an aqueous solution of the complex and filtering, the totality of Pd engaged (corresponding to a 5 wt.% theoretical metal loading) is incorporated within the solid in all cases, as evidenced by atomic absorption analyses of the filtrates. This was expected as the precursor exchanges its carboxylate ligands very easily and the number of surface oxygen groups are sufficiently high to incorporate 5 wt.% Pd in most cases. When less functions are available, some Pd⁰ is observed (see below, discussion of XPS characterization results) and again this is not unprecedented as Pd gets self-reduced on carbon surfaces, due to its noble character.

The solids have been washed on a Soxhlet apparatus, which led to Pd losses inferior to 0.2%, demonstrating that Pd is strongly adsorbed. The obtained solids have been analyzed by XPS (Table S4 in SI). The Pd atomic % measured at the surface of all samples prepared from supports of variable acidity was very similar (~0.7 at.%)

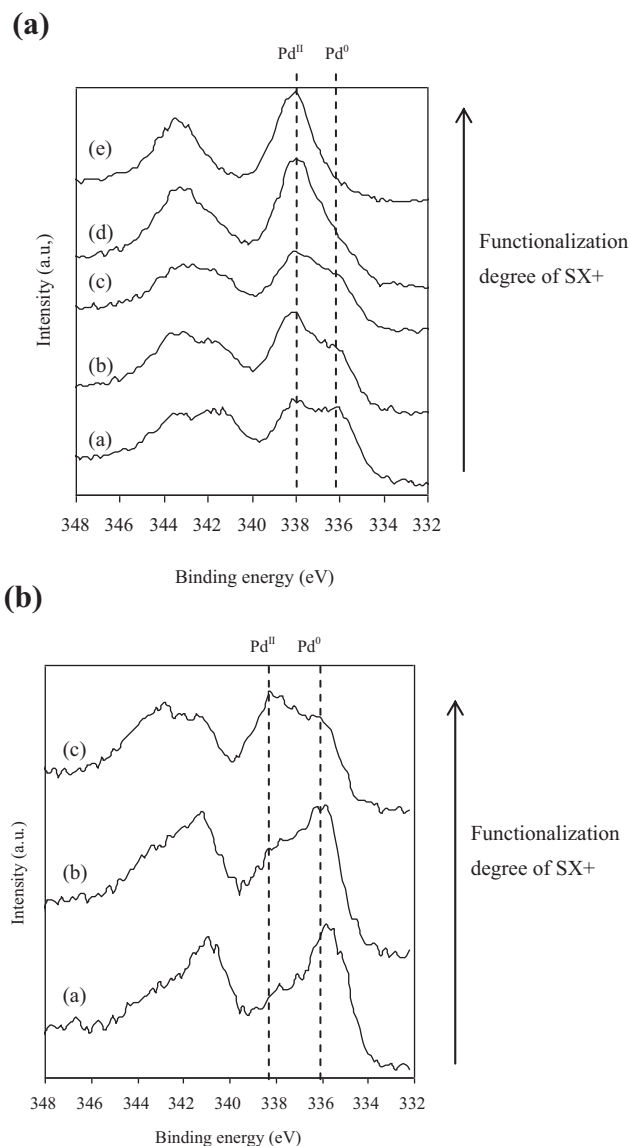


Fig. 4. (a) Pd3d XPS spectra for samples obtained by grafting (of [Pd(OAc)₂(Et₂NH)₂], in water at room temperature) on SX+ supports with different acidities. (a) SX+, (b) 0.2HNO₃-R, (c) 0.2HNO₃-R, (d) 1.0HNO₃-R and (e) 2.5HNO₃-R. (b) Evolution of degree of reduction of Pd (XPS) after thermal activation at 200 °C for Pd/C samples obtained by grafting (of [Pd(OAc)₂(Et₂NH)₂] in water at room temperature) on different SX+ supports (a) non functionalized, (b) 0.2HNO₃-R and (c) 2.5HNO₃-R.

and higher than calculated from the actual loading (0.59 at.%). This indicates that Pd grafting occurred more on the external surface than within the pores. This has been confirmed by grinding to expose the internal surfaces, leading to lower Pd at.% values. The specific surface area also diminishes due to pore blocking by the complex. Only the most functionalized support gives similar values, hence better homogeneity between surface and bulk, showing that its increased hydrophilicity has improved pore accessibility for the metal. At the surface, palladium was present as a mixture of Pd⁰ and Pd^{II} (Fig. 4(a)), except for the most functionalized carbons. If the complex was grafted by a neat ligand exchange mechanism, the Pd oxidation state should not change from the starting Pd^{II}. We believe therefore that the Pd^{II}/Pd⁰ ratio is a direct measure of the amount of complex actually grafted via oxygenated groups, with Pd⁰ being due to non-grafted complexes getting reduced by direct contact with the carbon surface. This is consistent with the fact that SX+ and mildly functionalized carbons do not present enough carboxylic acid functions (see Fig. 2) to graft the amount of Pd complex

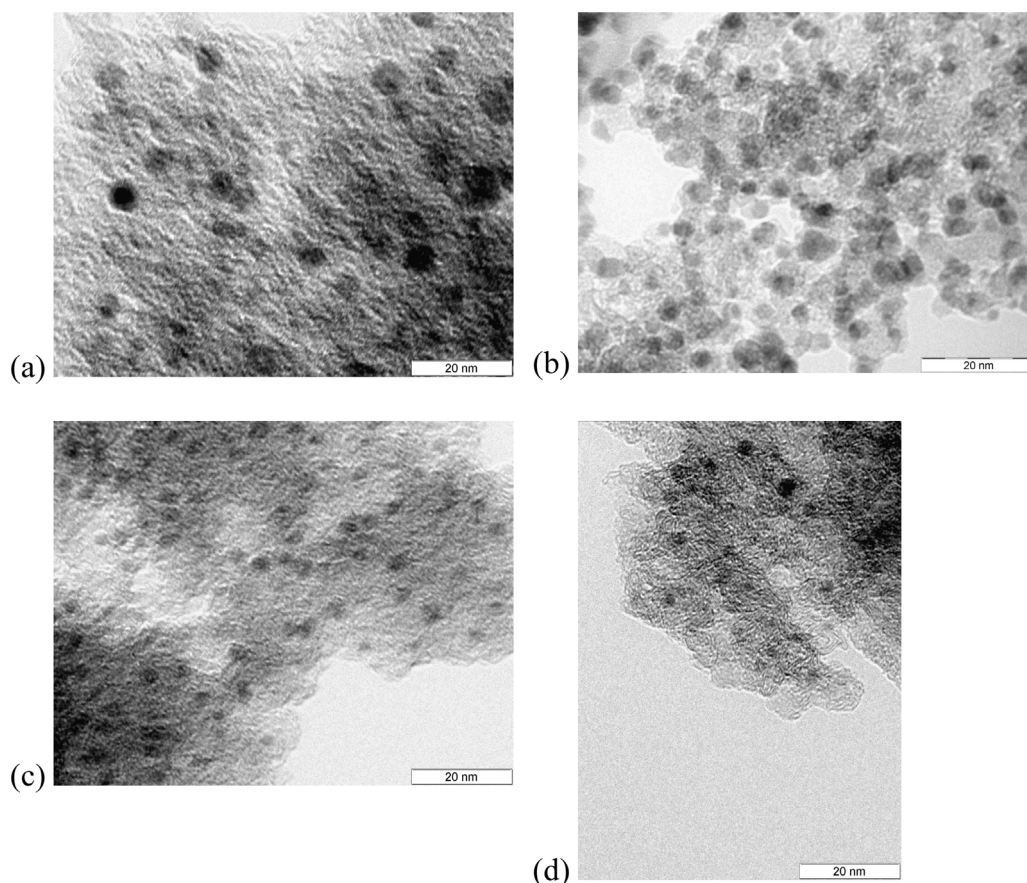


Fig. 5. TEM images of Pd/C samples prepared from $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ in water at room temperature and activated at 200 °C (a) on pristine SX+, (b) 0.2HNO₃-R, (c) 2.5HNO₃-R and (d) on stabilized support.

molecules incorporated (47 mmol/100 g_C). In this case, the nature of precursor–surface interactions is less clear: C=C bonds could play the role of alternative ligands [24]. The Pd^{II}/Pd⁰ ratio increases with the support acidity (Fig. 4(a)), indicating that the amount of grafting depends logically on the amount of available functions. The grafted fragments are stabilized against spontaneous reduction.

The N/Pd ratios increase with the support acidity (Table S4 in SI), in connection with the presence of nitro groups (see above). When considering N arising only from the complex (corrected by subtracting the amount of N in each starting carbon), the N_{corr}/Pd^{II} ratios are close to 1 (Table S4 in SI), in agreement with previously suggested models for the grafted fragments implying exchange of one carboxylate and one amine ligand for surface acidic groups [25,41].

With the support stabilized by heating (noted 2.5HNO₃-R-S), the 5 wt.% loading is also obtained, but the amount of Pd^{II} compared to Pd⁰ is smaller than with other supports treated with HNO₃ and slightly higher than with H₂O₂ (Table S4). This is related to the

nature of oxygenated functions on the surface, because –OH groups are less well suited than –COOH for grafting by carboxylate ligand exchange.

3.3. Activation

The grafted samples containing Pd molecular moieties immobilized onto the oxygen surface functions were activated thermally at 200 °C, in order to form supported Pd nanoparticles by coalescence. Even with the supports treated under identical conditions, this produces a new set of samples compared to those described previously [25], as those had been activated mostly at 500 °C. Grafting is supposed to improve final dispersion by hindering sintering during this step. Given that thermogravimetric analysis of the $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ complex under nitrogen shows complete ligand loss at 180 °C in one clean step, the activation was carried out at 200 °C under N₂ followed by H₂. This thermal treatment of the

Table 2

Activity in MNP for Pd/C catalysts prepared from $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ in water at room temperature and activated thermally at 200 °C.

Support ^a	Dispersion (%)	Activity in MNP (mmol/min g) expressed by			TOF (molec./min atomePd _{acc})
		g of catalyst	g of Pd	g of Pd ⁰	
SX+	7	0.664	13.28	16.36	24
0.2HNO ₃ -R	17	1.07	21.44	26.80	17
1.0HNO ₃ -R	25	1.12	22.32	33.32	14
2.5HNO ₃ -R	19	0.508	10.16	17.84	9
11.7H ₂ O ₂	10	1.03	20.56	24.77	25
2.5HNO ₃ -R-S	26	1.28	25.76	32.20	13

^a The functionalized supports are noted **R** when treated under reflux, **A** when using room temperature, **S** when stabilized, and the oxidant concentration (in mol L⁻¹) is specified besides its nature.

immobilized complex should thus lead to complete ligands removal with concomitant reduction of Pd^{II} into Pd^0 . The surface Pd concentration was found to decrease to ~ 0.4 at.% after heating under N_2 with no further change under H_2 (Table S5 in SI). A decrease in the amount of detected surface Pd can be related to the coalescence of Pd atoms. Indeed, as the depth of analysis of XPS is ~ 5 nm, when some Pd particles coalesce to reach nanoparticles with a diameter larger than 5 nm, some proportion of the Pd is not analyzed by the XPS method anymore. This was confirmed by TEM, which allow particles larger than 5 nm to be observed (see below). A mixture of Pd^{II} and Pd^0 was found at the surface with higher amounts of Pd^{II} when the support presented more acidic groups (Fig. 4(b)). This shows that the covalently grafted fragments are stabilized against reduction. This has already been observed by other authors even if phrased differently [42,43]. We believe that when this effect is not observed, the covalent nature of the precursor–surface interaction (i.e. actual grafting) can be questioned. It shows that grafting might be a disadvantageous preparation technique when aiming at reduced metals as active phase. Many authors claiming to use grafting did not check the Pd oxidation state before activation and might actually have improved the catalytic activity due to a side-effect of the preparation procedure (such as improved hydrophilicity thanks to surface functionalization) rather than thanks to real grafting.

The activated Pd/C samples have been imaged by TEM. In all cases, particle sizes were below 10 nm, homogeneously distributed, and varied with the support characteristics (Fig. 5). For pristine SX+ or H_2O_2 functionalized carbon, the particles were the biggest (~ 5 nm). They were smaller on HNO_3 functionalized carbon, and the smallest at 2–3 nm on the stabilized support. In the case of the stabilized support, some 20–40 nm particles were also observed. The very small particles must arise from fragments grafted on stable functions, while the bigger ones were probably formed by self-reduction and agglomeration for non-grafted molecules even before thermal activation. Indeed, less oxygen groups are available on the stabilized supports because the carboxylates have been removed, so some fraction of the complex might not be grafted properly and lead to these few agglomerates. Nevertheless, less particle growth was thus observed on average on the stabilized support because the most fragile functions were removed before grafting, thus coalescence of Pd atoms is controlled during thermal activation. No peaks could be observed by X-ray powder diffraction in all cases, by opposition to the samples activated at 500°C [25], in line with the small particle sizes.

The Pd dispersion was measured by CO chemisorption (Fig. 6(a)). It was found that the dispersion was always higher on functionalized supports (10–25%) compared to non-modified SX+ (7%) and the highest on the stabilized support (26%), in agreement with TEM observations.

When modifying the activation conditions, no benefit could be obtained (see Fig. S3). As already mentioned, increasing the temperature to 500°C led to worse dispersion and appearance of peaks in XRD diffractograms. Activating chemically with formalin or NaBH_4 increased the proportion of reduced palladium in the samples (higher %Pd⁰ observed by XPS), but did not give smaller Pd particles (TEM) or better dispersions (CO chemisorption).

3.4. Catalytic testing and discussion

The catalytic activity in the reduction of 2-methyl-2-nitropropane (MNP) in *t*-butylamine (TBA) (Scheme 1) is given in Table 2. When using only the carbon support (not loaded with Pd) as a 'blank' experiment, no MNP conversion higher than without catalyst was found. Moreover, the filtrates of catalytic tests were systematically analyzed for the presence of solubilized Pd. It was always lower than 1%.

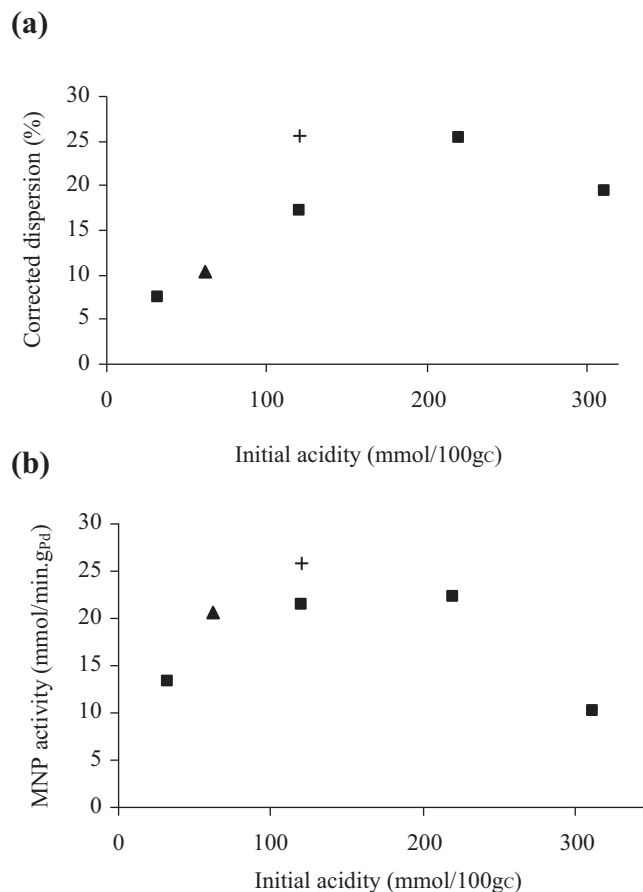


Fig. 6. (a) Correlation between dispersion and acidity of support: (■) HNO_3 functionalization, (▲) H_2O_2 functionalization, (+) stabilized support, for Pd/C samples prepared from $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ in water at room temperature. (b) Evolution of MNP activity in function of support initial acidity for Pd/C samples obtained by grafting (of $[\text{Pd}(\text{OAc})_2(\text{Et}_2\text{NH})_2]$ in water at room temperature) on (■) SX+ modified with HNO_3 or non-functionalized, (▲) SX+ modified with H_2O_2 , (+) stabilized SX+.

The activity varied with the support acidity (Fig. 6(b)), in a very similar fashion to the dispersion. The catalyst prepared on H_2O_2 -functionalized support is competitive: better than using the unmodified SX+ and better than expected on the basis of support acidity and dispersion. It presents the highest TOF value. The best catalyst of all in terms of activity expressed per gram of catalyst or g of Pd is the one prepared on the stabilized support, followed by 1.0 HNO_3 -R. The same conclusion is reached when looking at the results normalized by g of Pd⁰ (taken from XPS characterization).

In general, the functionalization/grafting strategy led to better dispersions, but the activity is not linearly correlated to that parameter, with catalysts prepared on highly functionalized supports showing a sharper decrease in activity. This can be related to several effects. First, the most functionalized samples are less well reduced. This is not the major factor, as the activity in MNP expressed by g of Pd⁰ for the catalyst prepared with the 2.5 HNO_3 -R support is lower than with the less functionalized supports. Second, the most functionalized supports being more hydrophilic, the metal grafting occurred more within the internal volume: the active phase within the smallest pores is maybe accessible to CO but not to the substrate in methanol during catalytic testing [44]. Third, a particle size effect is maybe playing a role with the smallest particles being too small for optimal activity. Finally, it has been shown that oxygenated groups present on the carbon support play an active role in the reaction [23]. Weak acidic groups were shown to have a beneficial effect while carboxylic acids are deleterious. Li et al. also observed a negative effect of support

functionalization by concentrated nitric acid in nitrobenzene hydrogenation, but an optimum for intermediate acidities [45].

We therefore believe that either functionalizing by H_2O_2 or using a HNO_3 -oxidized support that has been stabilized both lead to the same positive effects. First, these two strategies give in the final functionalized carbon supports a majority of weak acidic groupings such as phenols. Second, sintering is avoided during thermal activation as grafting occurred on the more stable functions rather than on thermally unstable carboxylic acids. Finally, a positive influence of weak acidic sites can also take place during catalysis. Taking all these advantages into account, it is by using the sequence HNO_3 /stabilization/grafting that the best results are obtained as higher amounts of oxygenated groups can be introduced on the surface. Indeed, H_2O_2 was considered as another option to introduce phenols rather than carboxylic acids on the surface, but when carrying out the functionalization, it decomposes over time when contacted with carbon. This hampers obtaining high functionalization rates with this reactant by playing with experimental variables such as longer reaction time during functionalization. Another option would be using air as oxidant, and this remains to be tested within the framework of the present study.

4. Conclusion

We have shown that it is possible to use oxygenated groups on active carbon surfaces to graft covalently carboxylate Pd complexes by ligand exchange. The amount of grafted metal can be evaluated from the $\% \text{Pd}^{\text{II}}$ present at the surface. This grafting preparation method is beneficial for obtaining very small Pd particles. Two drawbacks were identified for highly functionalized samples: (i) the difficulty in reducing the grafted samples and (ii) a deleterious effect of strong acidic groups during catalysis. Using H_2O_2 rather than HNO_3 for functionalization was shown to be favorable, but the best results were obtained on a HNO_3 -functionalized carbon that had been stabilized before grafting. The thermal stabilization procedure allowed removal of fragile carboxylic acid groups to leave mainly weakly acidic phenol groups. These acted therefore as more stable anchors for Pd grafting and higher metallic dispersion was obtained. The activity in 2-methyl-2-nitropropane (MNP) hydrogenation in *t*-butylamine (TBA) was thus enhanced, thanks to smaller Pd particles and the presence of weak acidic groups that seem to be beneficial for this reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.09.029>.

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