Topics in Catalysis (2020) 63:1485–1496
https://doi.org/10.1007/s11244-020-01376-y

ORIGINAL PAPER

Bimetallic Pd-Bi/C Catalysts Prepared by Grafting of Complexes with O-Donor Ligands

Chantal Diverchy[1] · **Vincent Dubois**[2] · **Michel Devillers**[1] · **Sophie Hermans**[1]

Abstract

Bimetallic carbon-supported PdBi catalysts were prepared by grafting. To do so a soluble complex of bismuth with exchangeable O-donor ligands was selected, and the carbon support was functionalized to increase the number of surface functions. The grafting procedure was carried out by contacting the various supports with solutions of Pd and/or Bi complexes, to allow ligand exchange reactions to take place between the complexes and the surface O-groups. The grafted fragments were then activated into carbon-supported nanoparticles, which were characterized to unravel the impact of grafting experimental variables on the physico-chemical characteristics of the materials obtained. The PdBi/C catalysts were finally tested in the archetypal glucose selective oxidation reaction, to assess the impact of those characteristics on the catalytic performance. It was found that simultaneous grafting gave larger nanoparticles than consecutive grafting, while higher number of stable surface functions allowed to obtain small and nicely distributed bimetallic nanoparticles. However, the surface functions were found to be deleterious for the catalytic activity, and the placement of the Bi promoter with respect to Pd active phase was identified as another key parameter for the activity, with grafting allowing to compare neatly samples where Bi is underneath, above or beside Pd.

Keywords Grafting · Bismuth · Carbon · Oxidation · Liquid phase

1 Introduction

For many heterogeneously catalyzed processes carried out in water or protic media, carbonaceous materials are unavoidable because other bulk or support materials are not stable under hydrothermal conditions [1, 2]. This is the case for example for carbohydrates that are efficiently catalytically transformed using carbon-supported catalysts in aqueous solution [3]. These sugar transformations might involve acidic sites for hydrolysis, dehydration or isomerization steps or metal nanoparticles for oxidation or hydrogenation. Each of these transformations has been studied since many years but bear current interest within the context of green and sustainable chemistry. Indeed, carbohydrates might be sourced out in lignocellulosic biomass and enter the so-called ‘biorefinery’ pathways [4, 5] to give high added-value platform compounds such as sorbitol, gluconic acid or hydroxymethylfurfural (HMF) [6].The cellulose part of lignocellulosic biomass is a polymer of glucose that can be depolymerized with strong acids. Glucose is then hydrogenated into sorbitol, oxidized into gluconic acid or dehydrated into HMF to name but a few [6].

In this general context, it has been shown that the addition of a post-transition elements to carbon-supported noble metals leads to enhanced catalytic properties [3, 7, 8]. In particular, bismuth and the bimetallic association Pd-Bi/C is very efficient for selective glucose oxidation into gluconic acid [9–11]. However, the surface chemistry and molecular interactions between the carbon surface and Bi-containing compounds has not been studied much. The Bi compounds envisaged as precursors in the preparation of such catalysts are not varied a lot and are very often added by deposition from a suspension in which they are not even soluble.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11244-020-01376-y) contains supplementary material, which is available to authorized users.

✉ Sophie Hermans
Sophie.Hermans@uclouvain.be

[1] Institute of Condensed Matter and Nanosciences (IMCN), UCLouvain, Place Louis Pasteur, 1, bte L4.01.03, 1348 Louvain-la-Neuve, Belgium

[2] Department of Physical Chemistry and Catalysis, LABIRIS, 1 Avenue Emile Gryson, 1070 Brussels, Belgium

When contacted with the carbon surface in a non-solubilizing medium, molecular interactions and strong bonds with the support cannot form and an inhomogeneous deposition occurs, governed by non-specific interactions. Pd/C materials are also used as electroctalysts in fuel cells (for example direct ethanol fuel cells (DEFC) or even direct glucose fuel cells (DGFCs)) and benefits from Bi added as promoter. For this application, again, Bi-Pd/C materials are prepared by simple methods that involve simple metal salts, usually chlorides. The more controlled so-called 'polyol' method, which consists in using ethylene glycol (EG) as a stabilizer and reducing agent, has been shown to be advantageous for electrocatalysts preparation [12, 13].

However, for transition metals, the molecular understanding of precursors/surface interactions is now very detailed and strategies such as grafting and anchoring are being used to increase the strength of surface binding [14]. Indeed, higher surface affinity leads unmistakably to higher dispersion and/or higher stability of the active phase. These procedures are therefore highly desirable for supported catalysts preparation. We define grafting and anchoring, as proposed by Lambert and Che [15], in the following manner: grafting is defined as the case where native surface groups of the support covalently bind to a metallic center and take part in its internal coordination sphere, thus acting as ligands, while anchoring is defined as the case where the metal atom of a complex is connected to the surface by a spacer arm via a series of covalent bonds. The latter require therefore an extra step to introduce such spacing arm on the surface, and grafting is preferred if at all possible.

Native surface groups are usually hydroxyls in the case of common inorganic oxides, such as silica or alumina. In the case of carbon, the surface might present some carboxylic acid, lactone and phenol groups of acidic nature, in various proportions, depending on the source. Those oxygenated groups can be increased by oxidation in liquid or gas phase. Each oxidant will preferably increase one type of O-group, for example hydrogen peroxide or air will increase phenolic groups, that are weakly acidic, while nitric acid treatment increases mainly carboxylic acids, that are strong acid sites [16]. Grafting is therefore difficult to achieve on standard carbonaceous solids used as catalytic supports, which are usually activated carbons, due to the initial low amount of O-groups. But when these have been increased by oxidation, surface ligand exchanges become possible, if the metal precursors are chosen adequately to allow for such facile ligand switch.

The goal of the present contribution is to explore the possibility of preparing Bi-based carbon-supported bimetallic catalysts by grafting, as this has remained mostly unexplored so far. In particular, we will attempt to prepare bimetallic Pd-Bi/C catalysts by grafting onto different carbon supports of varying acidity, that have been functionalized by nitric acid oxidation. We established the procedure for monometallic Pd/C formulations [17] and highlighted the ligand exchange mechanism in the case of palladium [18]. Here we need to find experimental conditions suitable for both metals. We selected a Bi compound that is easily solubilized and should readily exchange at least one of its ligands for surface O-group, namely Bismuth tris(dipivaloylmethanate) [$Bi(dpm)_3$], see Scheme 1. The challenge is therefore to introduce both metals in soluble form, and to allow for reactions with the carbon surface. To this end, we therefore compared consecutive or simultaneous grafting procedures, and the impact of other experimental variables (such as order of incorporation of the two metals in the case of consecutive grafting) on the physico-chemical characteristics of the solids recovered after filtration, but also of the final catalysts obtained after further activation. The obtained catalysts were tested in glucose selective oxidation into gluconic acid, as a model reaction for this bimetallic association, in order to observe the impact of such characteristics on catalytic performance. Preliminary account of this work has already appeared [19], as well as the simultaneous incorporation of both metals by using a single heterometallic compound [20]. A recent report studied the preparation of Pd-Bi catalysts supported on alumina, starting from soluble complex precursors with O-bonded ligands (Pd acetylacetonate and Bi acetate in that case) [21]. The authors found that combined impregnation gave the best results.

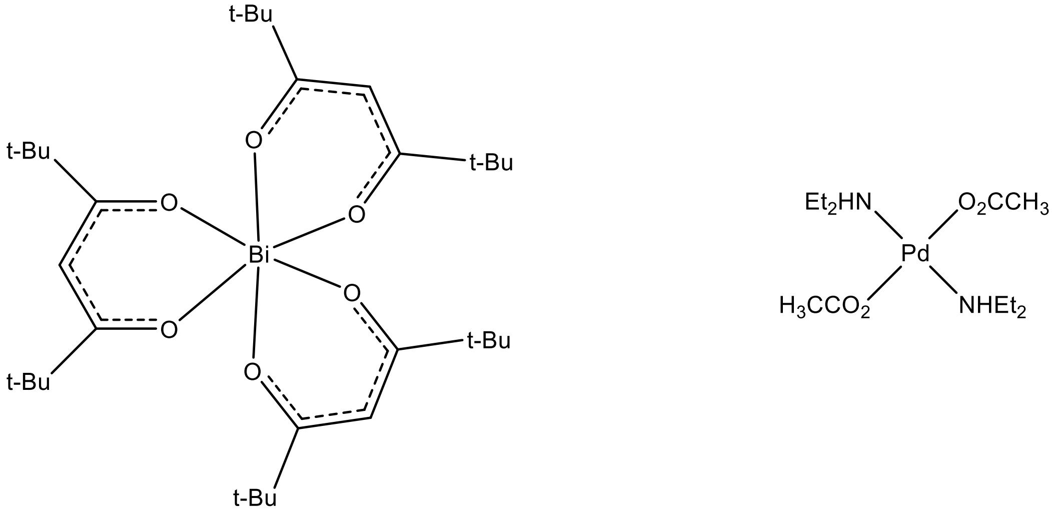
2 Experimental

2.1 Supports

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

Various functionalized carbon supports were prepared by oxidation by reaction with HNO_3 and characterized as detailed previously [17, 18]. The nitric acid concentration (0.2 or 2.5 mol/L) was varied to obtain several supports with different acidity. In short, functionalization was carried out by suspending 2 g carbon powder in 50 mL nitric acid in a three-necked round bottom flask equipped with a reflux condenser fitted with a trap filled with a base. The suspension was heated under reflux for 24 h. After reaction, the solid was filtered out, washed with distilled water, then extracted with water on a Soxhlet apparatus for 24 h, and dried at 50 °C for at least 4 h under vacuum. The functionalized supports are noted **R** when treated under reflux and the oxidant concentration is specified besides its nature.

Stabilized supports were obtained by heating the powders in a tubular oven at 500 °C for 8 h under nitrogen flux. The



Bismuth tris(dipivaloylmethanate)

[Bi(dpm)$_3$]

Diacetato bis(diethylamine) palladium

[Pd(OAc)$_2$(Et$_2$NH)$_2$]

Scheme 1 Structure of selected complexes

heating and cooling ramps were fixed at 100 °C/h. The letter **S** is added to the support name when stabilized.

Boehm's titration [22, 23] was used to evaluate the amount of carboxylic acid, lactone and phenol groups present at the surface of SX+ and functionalized carbon samples, by stirring 0.7 g of carbon in 50 mL NaOH. The carbon was filtered out after 24 h and the filtrate was titrated with hydrochloric acid using an appropriate color indicator (phenolphtaleine). All solutions were prepared using freshly distilled decarbonated water and maintained under nitrogen.

2.2 Grafting

Bismuth tris(dipivaloylmethanate) [Bi(dpm)$_3$] was purchased from Acros (Belgium) and used as received. It was characterized by infrared (IR) spectroscopy, elemental analysis (EA) and thermogravimetric analysis (TGA) to check its quality. The expected IR peaks were observed, with main bands being ν(C=O) at 1568 and 1533 cm^{-1}. EA: *Exp.* C 50.73 H 7.54 N 0.00% *Calc.* C 52.24 H 7.57 N 0.00%; TGA: *Exp.* 72%, *Calc.* 72% (Bi residue); 69% (Bi$_2$O$_3$ residue).

The [Pd(OAc)$_2$(Et$_2$NH)$_2$] complex was synthesized following a procedure from the literature [24]. Yield: 81%; IR: $\upsilon(\mathrm{COO})_{\mathrm{sym.}}$ 1374 cm^{-1}, $\upsilon(\mathrm{COO})_{\mathrm{asym.}}$ 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).

The engaged metal amounts of metal complexes in the grafting experiments with the supports were calculated to correspond to a theoretical 5 wt% loading in each metal. The actual loading in the final catalysts was determined by atomic absorption analysis of the grafting filtrates at the end of the procedure. In the case of the [Bi(dpm)$_3$] complex, grafting was carried out under inert atmosphere using Schlenk techniques to avoid side-reactions with water [25].

When grafting palladium in toluene, the [Pd(OAc)$_2$(Et$_2$NH)$_2$] complex (0.0348 g) dissolved in toluene (50 mL) and the selected carbon support (0.19 g) were stirred together for 24 h. This has been carried out at ambient temperature, 50 °C and under refluxing conditions with different (functionalized or not) carbon samples. After 24 h, the solid is recovered by filtration, washed abundantly with toluene, rinsed with acetone and finally dried under vacuum at 50 °C. The filtrate was evaporated to dryness and the solid residue dissolved in few ml aqua regia then diluted with distilled water in a 100 mL volumetric flask for further analyses.

When grafting palladium in water, 0.17 g [Pd(OAc)$_2$(Et$_2$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.

Simultaneous grafting has been carried out by dissolving 0.1742 g [Pd(OAc)$_2$(Et$_2$NH)$_2$] and 0.1815 g [Bi(dpm)$_3$] complexes in 50 mL degassed toluene and adding 0.90 g carbon support. After 24 h stirring at the fixed temperature under inert atmosphere, the solid was recovered by filtration, washed abundantly with toluene, rinsed with acetone and finally dried under vacuum at 50 °C. The filtrate was evaporated to dryness and the solid residue dissolved in few ml aqua regia then diluted with distilled water in a 100 mL volumetric flask for further analyses.

For consecutive grafting starting by palladium, 0.1742 g [$Pd(OAc)_2(Et_2NH)_2$] and 0.90 g carbon were first stirred in 50 mL at room temperature for 24 h. The solid is then filtered out, washed with water and dried under vacuum at 50 °C. The filtrate is kept for further analyses after dilution with distilled water in a 100 mL volumetric flask. Subsequently, 0.45 g of the dried solid [comprising the grafted fragment « $Pd(OAc)(Et_2NH)$ »] from the first step is suspended in 50 mL toluene with 0.0808 g [$Bi(dpm)_3$]. After 24 h stirring at the fixed temperature under inert atmosphere, the solid and filtrates were recovered as detailed above.

For consecutive grafting starting by bismuth, 0.0906 g [$Bi(dpm)_3$] and 0.45 g C are contacted for 24 h in 50 mL degassed toluene at room temperature under inert atmosphere. Then the solution is filtered. The solid is washed with toluene and acetone and dried under vacuum at 50 °C. The filtrate is evaporated to dryness and re-dissolved in aqua regia then diluted by distilled water in a volumetric 100 mL flask. The second step consists in contacting 0.45 g of the dry solid [considering to comprise the grafted « $Bi(dpm)_2$ » fragment] with 0.0758 g [$Pd(OAc)_2(Et_2NH)_2$] in 50 mL water. After 24 h stirring at room temperature, the solid is filtrated out, washed with distilled water and dried under vacuum at 50 °C. The filtrate is diluted to 100 mL in a volumetric flask for further analyzes.

In the case of consecutive grafting, the catalysts are noted M_1-M_2, where M_1 denotes the metal grafted in first position.

2.3 Activation

For thermal activation, the catalysts were heated in a Carbolite tubular oven (type STF 16/450) under nitrogen flow at 500 °C for 8 h. The samples were contained as thin layers in porcelain combustion boats.

For chemical activation, alternatively, the grafted samples were not filtered out. The suspension was heated at 80 °C and the pH increased at a value of 10 by adding NaOH 1 mol/L solution dropwise. Then, a known amount of formalin is added (about 1 mL for 1 g of carbon, in excess relative to the amounts of metals). If needed, the pH is readjusted at 10 by adding a diluted Na_2CO_3 solution. The mixture is stirred for 1 h at 80 °C. After cooling, the catalyst is recovered by filtration and abundantly washed with water. It is then dried under vacuum at 50 °C. The filtrate is concentrated at 100 mL for further analyses by using a rotating evaporator.

2.4 Catalytic Tests

All catalytic tests were performed in a thermostatized double-walled glass reactor equipped with an automatic titration device for pH control, as described previously [26]. The experimental conditions used for glucose oxidation can be summarized as follows: the stirring rate was fixed at 1000 rpm (mechanical stirrer); the temperature was fixed at 50 °C; the pH is continuously measured by a combined electrode AgCl/Ag (Beckman) and an automatic titrator (718 STAT TITRINO from Metrohm) adds a base (NaOH 5 mol/L) to keep the pH at the constant value of 9.2; oxygen is introduced in the solution at a constant flow rate of 0.4 L/min.

The tests are carried out with 400 mL milliQ water, 72 g glucose, 54 mg catalyst and for a duration of 4 h. The catalyst is recovered by filtration and washed with ethanol and ether. The filtrate is concentrated to 250 mL using a rotating evaporator for further analyses.

The composition of the reaction mixture arising from glucose oxidation was determined by ^{13}C-NMR analysis [9]. Although the formation of numerous secondary products is possible, the only carboxylic acid detected in the reaction media was gluconic acid, together with trace amounts of fructose produced by glucose isomerization. Hence, the catalytic performance was determined and compared based on the amount of NaOH added to neutralize the acids produced during the reaction, considering 100% selectivity for gluconic acid (fructose not titrated). The yield in gluconic acid is therefore directly calculated from NaOH consumption. The results are expressed in terms of conversion (X_{GLU}, %), or normalized activity defined as conversion per mg of Pd engaged in the test (X_{GLU}/m_{Pd} en %/mg). Blank tests with the support alone (functionalized or not) confirmed that these displayed no activity in this reaction.

2.5 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 containg 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 heating ramp under 100 mL/min nitrogen flow.

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

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

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,H component which was fixed at 284.4 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, with LA(1.9,7,2) asymmetric line shape, appears at Pd3d5/2 = 335 eV (Pd^0), while the second is 3 eV further for Pd^{II}. Constraints were also used for decomposing the Bi4f peak: area ratio (Bi4f7/2/ Bi4f5/2 = 1.33, difference in energy Bi4f7/2 − Bi4f5/2 = 5.31, FWHM = 1. A first doublet appears at Bi4f7/2 = 157 eV (Bi^0), while the doublet of oxidized species (Bi^{III}) is situated at Bi4f7/2 = 159 eV.

X-ray powder diffraction (XRD) analyses were carried out on a SIEMENS D5000 diffractometer equipped with a copper anticathode ($\lambda_{K\alpha} = 154.18$ 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.

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

The preparation of catalysts by grafting involves several steps: first an optional support functionalization procedure to increase the number of reactive surface groups that can act as ligands; then the actual grafting itself, consisting of a ligand exchange reaction between a solubilized complex and the surface functions of the support contacted in suspension; finally the catalyst activation by reducing the metal centers, which is accompanied by ligands removal and nanoparticles formation. We followed this procedure first for each metal separately, and then together, and characterized the solids obtained before engaging them in catalytic testing, in order to assess the impact of several key experimental variables on grafting and therefore on materials characteristics and performance.

Therefore, the selected support, an activated carbon from Norit (SX+), was first oxidized in order to increase the number of its oxygenated surface functions. The starting carbon has an acidity (determined by Boehm titration) of 28 mmol/100 g C that increases to 116 or 311 mmol/100 g C when treated by HNO_3 0.5 or 2.5 mol/L under reflux for 24 h, respectively. The specific surface area remains constant for the mild treatment but decreases slightly from 922 to 756 m^2/g when using the most concentrated acid solution. This gives a final density of 248 acid sites per 100 nm^2 (see Table S1 in Supplementary Information (SI)).

The different supports with varying amounts of acid groups were contacted with solutions of Bi and/or Pd complexes bearing oxygenated ligands (Scheme 1), to allow for ligand exchange reactions. If the initial complexes exchange their ligands for surface O-group, they become coordinatively bound to the surface, which is the definition of grafting. This should allow for optimal dispersion and stabilization of the active phase during activation. Indeed, the metallic ions need to be stripped of their ligands and reduced into the metallic phase to give the active catalysts. We will compare both thermal and chemical activation, the latter permitting to avoid high temperature treatment. Thermogravimetric analysis was used to confirm that both complexes decompose cleanly into Pd or Bi metal, with no other residue remaining from the ligands.

The $[Bi(dpm)_3]$ complex was selected as Bi precursor because the β-diketonate ligands should exchange readily for surface oxygenated functions and it would avoid surface contamination by elements other than C, O, H. Bismuth carboxylates were discarded because of their low solubility [27]. The $[Bi(dpm)_3]$ complex is soluble in aprotic organic solvents, and was grafted in toluene. 100% incorporation was obtained (i.e. 5 wt% Bi) when grafting Bi alone in toluene at 25 or 120 °C. No Bi^0 was detected at the surface by XPS, but only Bi^{III}, proving that the desired ligand exchange for surface functions occurred successfully. No metal leaching was observed during extensive washing in a Soxhlet apparatus proving the strength of the bond with the surface.

The Pd complex grafting in water has been optimized previously [17, 18]. Here, we explored Pd grafting in toluene to be compatible with the Bi precursor. First, the selected $[Pd(OAc)_2(Et_2NH)_2]$ complex was contacted with SX+ or functionalized carbon in toluene at different temperatures (see Table S2 in SI). At room temperature, the amount of Pd incorporated on unmodified SX+ is only 24% of the quantity engaged. Under refluxing conditions, it is > 90%, and it reaches intermediate value at intermediate temperature. On the functionalized support, it is always > 95%, even at room temperature. However, the % amount of surface Pd^{II}, which we found indicative of the % of grafting via ligand exchange [17, 18], decreases when the temperature increases (Table S2 and Figure S1). It is also higher on functionalized support than on pristine SX+. Grafting by ligand exchange is obtained when using low temperature and/or functionalized support, as indicated by N/Pd ratio ≈ 1 [17, 18] (Table S2). When the complex is grafted, it is present as a $[Pd(OAc)(Et_2NH)]$ fragment, but when there is no grafting, self-reduction occurs on the surface due to the noble metal character of Pd. The fact that Pd is more difficult to graft in toluene than in water is probably due to the fact that toluene might compete for adsorption on the hydrophobic surface [28, 29].

Bimetallic catalysts were prepared first by simultaneous grafting of both Pd and Bi complexes in toluene under reflux. Refluxing conditions were necessary to ensure that all Pd amount would be incorporated on the supports. Indeed, atomic absorption analyses of the filtrates after grafting experiments confirmed that both metals were loaded totally in these conditions, to give a 10 wt% total metal loading. These samples were activated either thermally or chemically and the results of XPS characterization before and after activation are given in Table 1. The atomic percentages in each analyzed element were obtained from narrow scans, in the best binding energy window for each. The measured surface atomic ratios decrease when the acidity of the support increases. We ascribe this to a modification of particles sizes hence of dispersion on the surface. Even before activation, a high proportion of both metals were already in their reduced state. The surface atomic ratios were found to decrease during activation, but more during thermal than chemical activation, to reach in both cases Bi/Pd ratios ≈ 1. This means that heating causes sintering and also Bi surface enrichment. SEM imaging of the obtained catalysts revealed the presence of particles ~ 20 nm in size on the external surface (Fig. 1). Bigger particles are obtained by thermal than by chemical activation. This is coherent with XPS results and it is explained by occurrence of auto-reduction in refluxing toluene. Indeed, similar images were already obtained before activation (Fig. 1). However, larger agglomerates are obtained on SX+ than on functionalized support, indicating that the oxygenated groups played their stabilizing role against agglomeration. XRD analyses indicated the presence of $BiPd_3$ and Pd in catalysts activated thermally, while no intermetallic compound was detected in the samples activated chemically.

Table 1 XPS results for Pd-Bi/C catalysts obtained from $[Pd(OAc)_2(Et_2NH)_2]$ and $[Bi(dpm)_3]$ simultaneously in toluene under reflux

	XPS	Support		
		SX+	$0.2HNO_3$-**R**	$2.5HNO_3$-**R**
Before activation	% at. Pd	3.00	2.07	1.52
	% at. Bi	2.52	2.38	0.58
	Bi/Pd	0.84	1.15	0.38
Thermal activation	% at. Pd	1.57	0.71	1.00
	% at. Bi	1.91	0.98	1.14
	Bi/Pd	1.22	1.38	1.14
Chemical activation	% at. Pd	2.91	1.33	1.25
	% at. Bi	2.77	1.73	0.63
	Bi/Pd	0.95	1.30	0.50

Given these results, consecutive grafting was carried out by grafting Pd in water and Bi in toluene. This allows working at room temperature for both metals and should lessen spontaneous reduction. The order of incorporation was varied. Table 2 shows that 100% incorporation was nearly always obtained, except in the cases were the support is not or mildly functionalized and Bi is incorporated first. In these cases, Bi grafting hinders optimal Pd grafting. When the support is functionalized (regardless of the incorporation order), the surface atomic percentages in each metal determined by XPS are lower than with unmodified SX+. This probably indicates better access to the pores with more hydrophilic supports. In all cases, surface enrichment in bismuth was observed, even when incorporated in second position. This is due to its lower surface energy than Pd [30]. Most of the Pd was already reduced before activation, but less with functionalized supports (see Figure S2 in Supplementary Information, with Table giving % Pd^{II} numbers), indicating the positive role of increasing the number of oxygenated groups to increase the proportion of grafting by ligand exchange. The same effect is observed for bismuth (see numbers of % Bi^{III} in Figure S2) although it is far less reduced than Pd, in line with the noble metal character of the latter. After activation, the amount of reduced Pd increases (Figure S3, with Table giving % Pd^{II} numbers), while bismuth on the surface remains mostly oxidized (% Bi^{III}, Figure S3). In

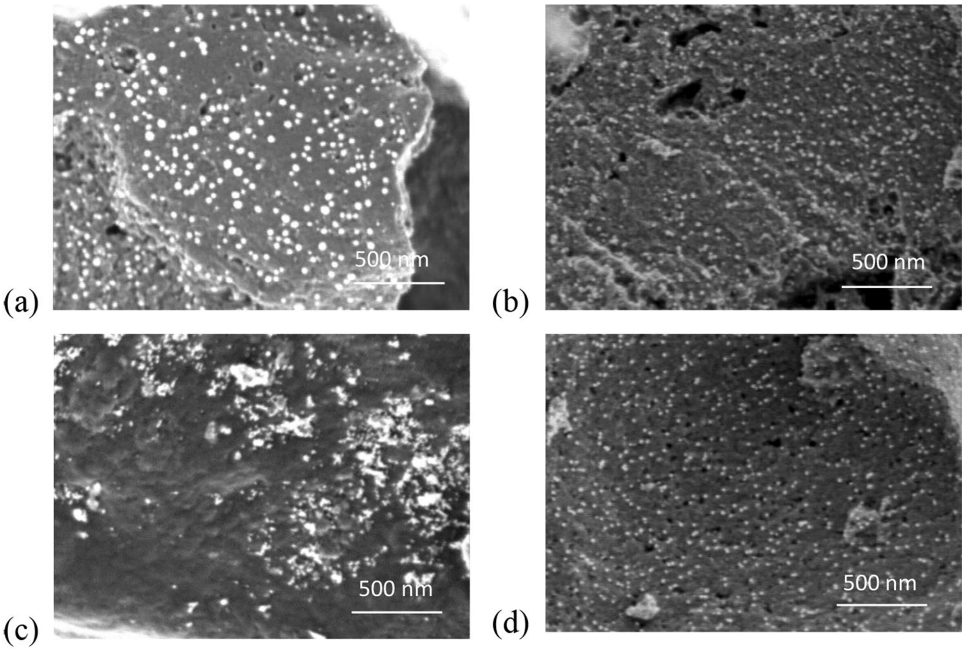


Fig. 1 SEM images of Pd-Bi/C samples obtained by simultaneous incorporation in toluene under reflux from [$Pd(OAc)_2(Et_2NH)_2$] and [$Bi(dpm)_3$] on 2.5HNO_3-R support **a** activated thermally at 500 °C or **b** chemically by formalin. Samples before activation prepared on supports **c** SX+ and **d** 2.5HNO_3-R

Table 2 Loading and XPS analyses for PdBi/C samples obtained by consecutive grafting of [$Pd(OAc)_2(Et_2NH)_2$] in water and [$Bi(dpm)_3$] in toluene at room temperature

Order	Support	% loaded[a]		XPS before activation			XPS after thermal activation		
		Pd	Bi	% at. Pd	% at. Bi	Bi/Pd	% at. Pd	% at. Bi	Bi/Pd
Pd-Bi	**SX+**	100	100	1.26	3.75	2.98	0.54	0.56	1.04
	0.2HNO_3-**R**	97	100	0.63	1.68	2.65	0.53	0.51	0.95
	2.5HNO_3-**R**	100	100	0.66	0.65	0.98	0.41	0.35	0.85
Pd-Bi	2.5HNO_3-**R**-S	~100	~100	0.57	3.80	6.68	0.35	0.41	1.18
Bi-Pd	**SX+**	91	100	0.66	2.71	4.11	0.66	2.54	3.84
	0.2HNO_3-**R**	92	100	0.56	1.03	1.84	0.36	0.30	0.82
	2.5HNO_3-**R**	100	100	0.69	0.44	0.64	0.37	0.25	0.67

[a] Determined by atomic absorption of syntheses filtrates, the 100% maximum corresponds to 5 wt%

addition, the XPS surface atomic % in each metal decreases and the Bi/Pd ratios become ≈ 1 (Table 2). The metal atoms become thus mobile and rearrange during activation. TEM images show that, by opposition with simultaneous grafting, consecutive grafting gave very small nanoparticles homogeneously distributed after activation (Fig. 2). In the case of functionalized support, small particles 3–7 nm in size were obtained (Fig. 2b). Functionalization is essential to avoid agglomeration (Fig. 2a), but the order of incorporation did not influence strongly particle size (Fig. 2c). The X-ray powder diffractograms of the activated materials were featureless in line with the small particles size obtained and is thus not useful to determine if alloying occurred during activation or not. However, EDXS spectra taken in different zones of the activated samples indicated the simultaneous presence of both Bi and Pd in all places (Figure S4). In addition, the Pd3d XPS peak was shifted toward higher binding energies, indicating the presence of intermetallic compounds (Fig. 3) [31]. These two metals are highly miscible, as confirmed by their binary phase diagram [32], displaying many mixed phases, hence alloying is expected. Moreover, the % Pd^{II} has dropped to 0% in the bimetallic sample (against 34% in the monometallic one), as a further proof of alloying.

To limit metal atom mobility during activation, one support was stabilized by removing the most fragile oxygenated groups by heating under inert atmosphere the most functionalized carbon (obtained in nitric acid 2.5 mol/L) before introducing the metals. The temperature of this preliminary heat-treatment was chosen as the same as the subsequent activation temperature for the metals, to remove fragile groups that—if used up for grafting—would get damaged during activation and provoke sintering of liberated metal atoms. The acidity of this new support was obviously lower after stabilization: 126 mmol/100 g against 311 mmol/100 g C before heating (see Table S1), which is by coincidence very similar to the sample obtained in nitric acid 0.2 mol/L, but now with a majority of stable functions (phenols) rather than mainly carboxylic acids [18]. However, it is still much

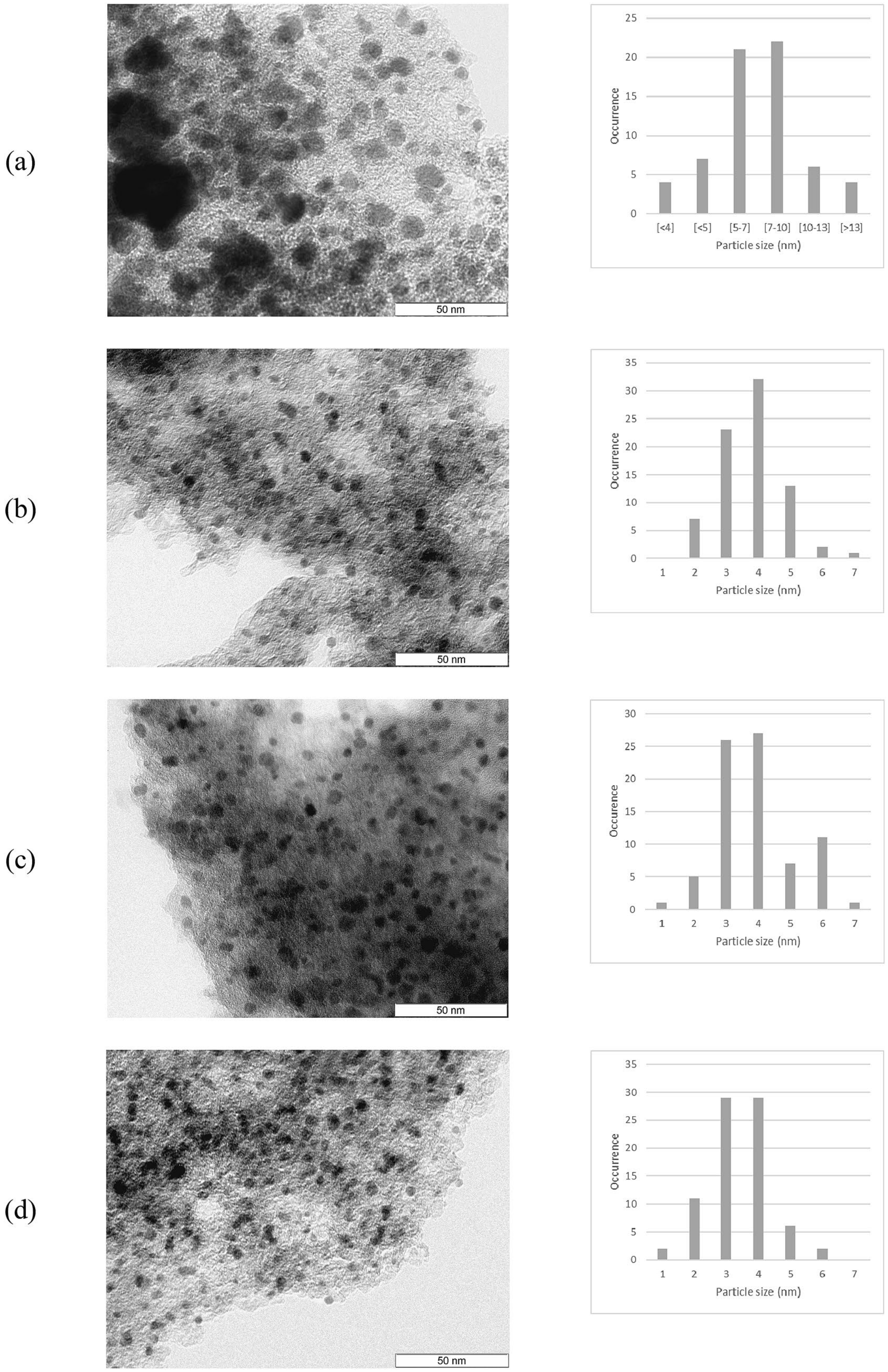


Fig. 2 TEM images of bimetallic catalysts prepared by consecutive grafting of [Pd(OAc)$_2$(Et$_2$NH)$_2$] in water and [Bi(dpm)$_3$] in toluene: **a** Pd-Bi on unmodified SX+, **b** Pd-Bi on 2.5HNO$_3$-R and **c** Bi-Pd on 2.5HNO$_3$-R and **d** Pd-Bi on stabilized support 2.5HNO$_3$-R-S

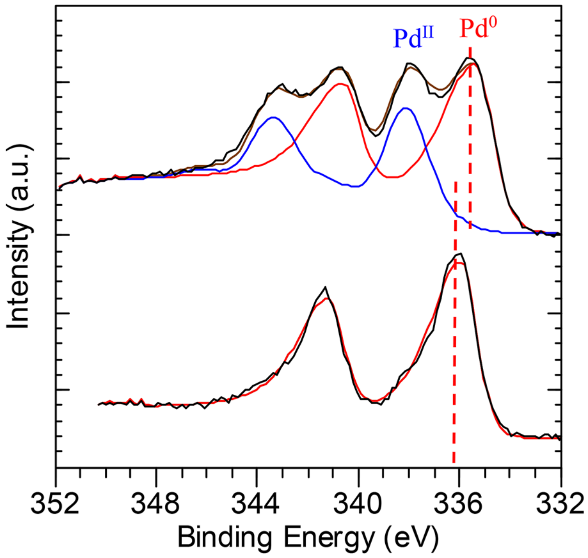


Fig. 3 XPS Pd3d peak for (top) Pd/C monometallic catalyst prepared by grafting of [$Pd(OAc)_2(Et_2NH)_2$] in water and of (bottom) bimetallic Pd-Bi/C catalyst prepared from [$Pd(OAc)_2(Et_2NH)_2$] in water and [$Bi(dpm)_3$] in toluene; in both cases on non-functionalized SX+ support

	% Pd^{II}
Top	34
Bottom	0

higher than the starting SX+ carbon (28 mmol/100 g C, see Table S1), thus grafting will still be possible. The stabilized support (noted **S**) was therefore used for consecutive grafting of Pd and Bi at room temperature. The bimetallic catalyst obtained presents the smallest particles (3–4 nm, Fig. 2d), demonstrating clearly the positive influence of stable function underneath the metal sites and the advantage of grafting. The atomic % in Bi and Bi/Pd ratios measured at the surface by XPS were very high before activation but decreased strongly during activation (Table 2). Again, no peak was observed in the X-ray diffractogram, but EDXS proved intimate mixing of both metals (Figure S4). A few 40 nm agglomerates were nevertheless observed by SEM due to the fact that there are not enough O-groups remaining to graft 10 wt% total metal.

In order the discriminate the different materials, and observe the influence of the preparation method, catalytic tests were carried out for the archetypal reaction of glucose selective oxidation into gluconic acid. The supports alone (unmodified SX+ of functionalized carbons) do not give any conversion in glucose oxidation. The known synergistic effect for this bimetallic association was obtained with monometallic Bi/C formulations being completely inactive, monometallic Pd/C moderately active and bimetallic PdBi/C giving highly performant catalysts. In all cases, the only product observed was gluconic acid, and the parallel evolution of conversion allows for direct comparisons. Hence the catalytic results after 4 h were normalized with respect to the amount of Pd (active phase) in the catalysts and plotted as a function of carbon support acidity. This is shown in Fig. 4.

In the case of simultaneous grafting, the samples activated thermally display a catalytic activity that decreases with increasing support functionalization. This could be due to a deleterious effect of the surface functions on the catalytic mechanism and also of a particle size effect. It was indeed observed that particle sizes decreased with increased support functionalization (see above). The particle size effect observed here is therefore the inverse trend of what is generally accepted in heterogeneous catalysis: smaller particles lead to poorer performance. This is actually known in this reaction and ascribed to stronger poisoning of smaller particles by oxygen [33].

By opposition to thermal activation, all catalysts activated chemically present mediocre performance. This might be ascribed to the strength of the surface O–M bonds formed by grafting that stabilize the metal centers against reduction and nanoparticles formation; the conditions of chemical activation being therefore too mild to counteract this effect. The absence of intermetallic compounds in the samples activated chemically (see above, XRD results) corroborates this statement and might explain low performance. Indeed both metals need to be in close contact to obtain the desired synergetic effect.

In the case of consecutive grafting, the catalytic activity was strongly influenced by the order of incorporation, with catalysts prepared by grafting Pd first giving best results. The activity was also influenced by the supports acidity, mainly in the cases where Bi had been grafted in first position. The catalyst obtained on stabilized support gave an activity similar to the sample prepared on non-stabilized support of similar final acidity: $X_{GLU}/m_{Pd} = 10$ (%/mg). It is thus the number of oxygenated groups, rather than their nature, or the final particle size obtained, that plays a major role for catalytic performance.

In this reaction, as stated above, small Pd particles have been shown to deactivate quickly due to oxygen poisoning [33]. It is widely admitted that oxygen poisoning is the main cause of deactivation for Pd in glucose oxidation.

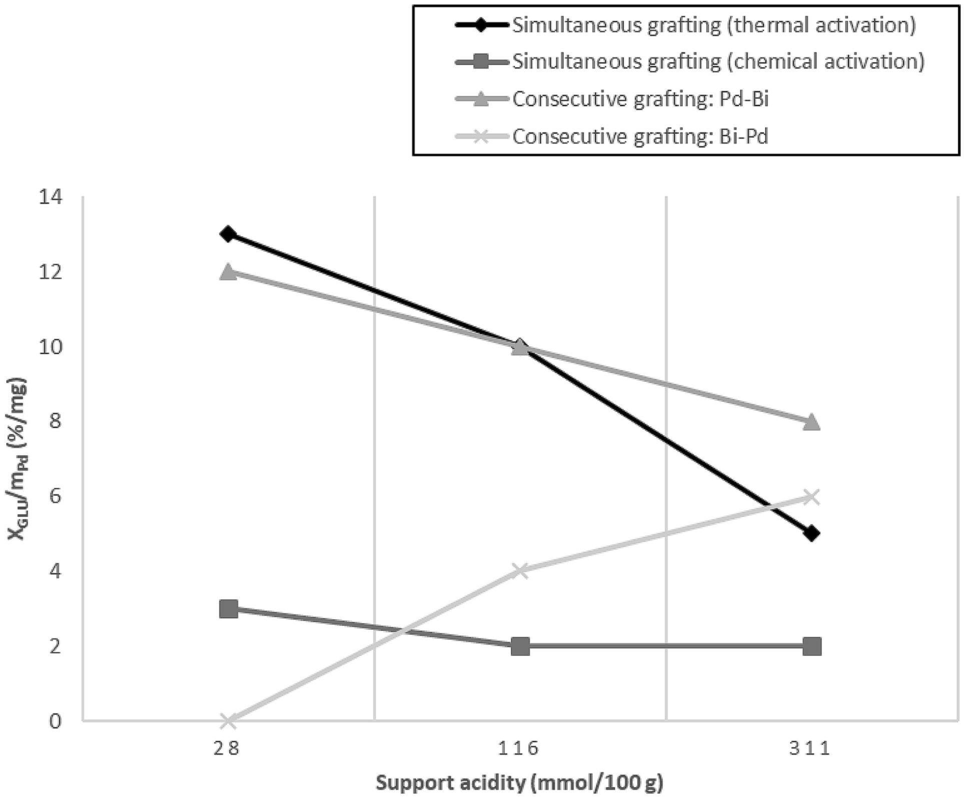


Fig. 4 Normalized catalytic activity (glucose conversion per mg of Pd) as a function of support acidity for bimetallic catalysts prepared by grafting

The role of bismuth as promoter is to act as a co-catalyst to avoid this phenomenon thanks to its higher affinity for oxygen. Hence Bi atoms placed above Pd are the ideal local structure for the active sites [10]. It is known that the best catalysts in glucose oxidation are those where Bi covers Pd [34]. This explains why the catalysts prepared by grafting Pd first and Bi second are much more active than the reverse order.

It also explains the deleterious effect of increasing acidity for Pd-Bi samples (Pd grafted first): when the number of oxygen groups increases, the amount of Bi in direct interaction with the carbon support rather than with Pd increases. Better grafting of both metals can occur because more anchoring points are available and they are not all used up by the first one that is contacted with the support. This gives smaller particles because metal grafted fragments are stabilized against sintering during activation. However, smaller particles are not advantageous for this reaction, as explained above and also observed on the similar work carried out on alumina for this same reaction [21]. Indeed, Sandu et al. [21] also observed that combined impregnation of Pd and Bi complexes gave larger particles than in the Pd-Bi/Al_2O_3 sample prepared by sequential impregnation. However, combined impregnation lead to closer proximity between both metals (more bimetallic particles) and higher conversion and selectivity in glucose oxidation than sequential impregnation, in line with our results.

Finally, the opposite trend was observed for Bi-Pd samples (Bi grafted first): increased acidity gave better performance (Fig. 4). Again, this makes perfect sense with what is known about catalyst structure ideal for this reaction. At low acidity, not enough functions are available and Pd will not be fully grafted onto C–O groups, but some palladium will cover the bismuth. With increasing surface functionalities, both metals might be grafted side by side and rearrange into the active Bi-covered Pd sites during activation, thanks to the lower surface energy of Bi [30]. However, even with the most functionalized support, the Bi-Pd/C sample obtained does not outperform the Pd-Bi/C catalysts prepared in the reverse order. All trends are therefore fully explained. This demonstrates how catalysts prepared by a controlled fashion allow to unravel subtle effects in catalytic reactions. The methodology developed in the present contribution could easily be applied to other catalytic systems where Bi is used as a promoter. The chosen complex indeed allows to carry out grafting in a neat fashion and gives model catalysts where bismuth can play its promoter role. The advantages of this newly considered Bi complex is that it is commercial, highly soluble, does not contain any other heteroatom, and is activated cleanly, allowing wide applicability, obviously to other supports as well.

4 Conclusion

In this work, we developed a methodology to prepared Bi-promoted catalysts by grafting. A soluble Bi complex was selected as grafting involves ligand exchange reactions between soluble metal complex precursors and the surface functional groups of the solid support. The bimetallic PdBi/C system applied in glucose selected oxidation into gluconic acid was selected as archetypal catalyst to unravel structure/activity relationships. Indeed, grafting will influence strongly the physico-chemical characteristics of the obtained catalysts and several key experimental variables were explored to evaluate their influence on such characteristics and therefore on catalytic performance: consecutive vs. simultaneous grafting, order of incorporation in the case of consecutive grafting, temperature of the solution during grafting reaction, etc. The bimetallic PdBi/C materials prepared by grafting were activated, characterized and tested in glucose oxidation. Several carbon supports of increasing acidity were compared, which have been prepared by nitric acid functionalization and characterized by Boehm titration.

It was found that the grafting mechanism indeed occurs by ligand exchange for surface O-groups, and stabilizes the metal centers in oxidized form. The chosen Bi complex was demonstrated as ideal to obtain successful grafting and allows introducing the Bi promoter without any contaminants. Small and bimetallic nanoparticles homogeneously distributed over the support were obtained in the case of consecutive grafting at room temperature, and the particles were smaller when the number of surface O-groups was increased. The smallest particles were obtained when using a support with stabilized surface functions. The oxygenated groups indeed act as anchoring points for the metal complexes, and cause lower ion mobility during activation, and more so if there are stable themselves. Simultaneous grafting could not be carried out at room temperature hence gave much larger particles due to self-reduction of palladium under refluxing conditions (Pd being a noble metal and carbon an electron-rich surface). The number of surface O-groups was also found to influence strongly the catalytic performance. This was ascribed to two effects: the strong adsorption of sugar molecules on those sites rather than on metal nanoparticles, and the stabilization of grafted fragments that do not allow the formation of intermetallic compounds and intimate mixing of both metals. In addition, the order of incorporation in the case of consecutive grafting was also found to strongly influence the performance, with catalysts prepared by grafting first Pd and then Bi being much more active than the reverse order. This allows the ideal active site to consist in Pd nanoparticles being covered by bismuth to avoid Pd poisoning by oxygen.

Acknowledgements The authors wish to thank the Fonds de la Recherche Scientifique (FRS-FNRS) with the assistance of the Fédération Wallonie-Bruxelles and the Belgian National Lottery, as well as the Université catholique de Louvain for funding. This work was also partially funded by the Belgian State (Belgian Science Policy, IAP Project INANOMAT N° P6/17). We are grateful as well to NORIT for the supply of SX+ activated carbon and to Jean-François Statsyns for technical assistance. We are also extremely grateful to Pierre Eloy for useful discussion and assistance for XPS data interpretation.

Author Contributions Conceptualization: [MD, SH], Methodology: [CD, SH], Formal analysis and investigation: [CD, SH], Writing—original draft preparation: [CD, VD, SH]; Writing—review and editing: [SH], Funding acquisition: [MD, SH], Resources: [MD, VD], Supervision: [MD, SH].

Funding This work was financially supported by the Fonds de la Recherche Scientifique (FRS-FNRS), the Fédération Wallonie-Bruxelles and the Belgian National Lottery, as well as the Université catholique de Louvain. This work was also partially funded by the Belgian State (Belgian Science Policy, IAP Project INANOMAT N° P6/17).

Data Availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Code Availability Not applicable.

Compliance with Ethical Standards

Conflict of interest The authors have no conflict of interest to declare.

References

1. Serp P, Figueiredo JL (eds) (2008) Carbon materials for catalysis. Wiley, New York. Print ISBN: 9780470178850
2. Rodriguez-Reinoso F (1998) Carbon 36:159–175
3. Besson M, Gallezot P (2000) Catal Today 57:127
4. Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick WJ Jr, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T (2006) Science 311:484–489
5. Parajuli R, Dalgaard T, Jørgensen U, Adamsen APS, Knudsen MT, Birkved M, Gylling M, Schjørring JK (2015) Renew Sustain Energy Rev 43:244–263
6. Yabushita M, Kobayashi H, Fukuoka A (2014) Appl Catal B Environ 145:1–9
7. Blaser HU, Indolese A, Schnyder A, Steiner H, Studer M (2001) J Mol Catal A Chem 173:3
8. Mallat T, Baiker A (1994) Catal Today 19:247–284
9. Wenkin M, Touillaux R, Ruiz P, Delmon B, Devillers M (1996) Appl Catal A Gen 148:181–199
10. Besson M, Lahmer F, Gallezot P, Fuertes P, Flèche G (1995) J Catal 152:116–121
11. Ablasser C, Hilger A, Hinrichsen O (2014) Chem Ing Tech 86:1948–1953
12. Cai J, Huang Y, Guo Y (2013) Electrochim Acta 99:22–29
13. Chen C-C, Lin C-L, Chen L-C (2015) J Power Sources 287:323–333

14. de Jong KP (ed) (2009) Synthesis of solid catalysts. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p 422. ISBN: 978-3-527-32040-0
15. Lambert JF, Che M (2001) In: Centi G, Wichterlová B, Bell AT (eds) Catalysis by unique metal ion structures in solid matrices. NATO science series, II: mathematics, physics and chemistry, vol 13. Kluwer Academic Publishers, Dordrecht, p 1
16. Yang X, Wan Y, Zheng Y, He F, Yu Z, Huang J, Wang H, Sik Ok Y, Jiang Y, Gao B (2019) Chem Eng J 366:608–621
17. Hermans S, Diverchy C, Dubois V, Devillers M (2014) Appl Catal A Gen 474:263–271
18. Hermans S, Diverchy C, Demoulin O, Dubois V, Gaigneaux EM, Devillers M (2006) J Catal 243:239–251
19. Diverchy C, Hermans S, Devillers M (2010) Stud Surf Sci Catal 175:703–706
20. Li B, Zhang H, Huynh L, Diverchy C, Hermans S, Devillers M, Dikarev EV (2009) Inorg Chem 48:6152
21. Sandu MP, Sidelnikov VS, Geraskin AA, Chernyavskii AV, Kurzina IA (2020) Catalysts 10:271–292
22. Boehm H-P, Diehl E, Heck W, Sappok R (1964) Angew Chem Int Ed 3:669
23. Polania-L A, Papirer E, Donnet JB, Dagois G (1993) Carbon 31:473
24. Hermans S, Wenkin M, Devillers M (1998) J Mol Catal A Chem 136:59–68
25. Pisarevskii AP, Martynenko LI, Dzyubenko NG (1992) Zh Neorg Khim 37:72
26. Wenkin M, Ruiz P, Delmon B, Devillers M (2002) J Mol Catal A Chem 180:141–159
27. Pisarevskii AP, Martynenko LI, Dzyubenko NG (1990) Zh Neorg Khim 35:1489
28. Van Dam HE, Van Bekkum H (1991) J Catal 131:335
29. Wibowo N, Setyadhi L, Wibowo D, Setiawan J, Ismadji S (2007) J Hazard Mater 146:237
30. Miedema AR (1978) Z Metallked 69:H.5
31. Miyake T, Asakawa T (2005) Appl Catal A 280:47
32. Okamoto H (1994) J Phase Equilib 15:191
33. Besson M, Gallezot P, Lahmer F, Flèche G, Fuertes P (1993) In: Kosak JR, Johnson TA (eds) Catalysis of organic reactions. Dekker, New York, p 169
34. Mallat T, Baiker A (1991) Appl Catal A 79:41