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Hydrogenation of nitrobenzene over Pd/C catalysts prepared from molecular carbonyl–phosphine palladium clusters

Christopher Willocq^a, Vincent Dubois^b, Yaroslav Z. Khimyak^{c,1}, Michel Devillers^a, Sophie Hermans^{a,*}

^a Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur 1/3, B-1348 Louvain-la-Neuve, Belgium

^b Laboratoire de Chimie Physique et Catalyse, Institut Meurice, Avenue Emile Gryzon 1, 1070 Bruxelles, Belgium

^c Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom

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1. Introduction

The major drawback of heterogeneous catalysts in general is their inhomogeneous surface comprising different types of catalytic sites, with for example metal centers being in different chemical, electronic and/or geometrical states [1]. This might lead to poor selectivity, especially when compared to homogeneous systems. Numerous studies have been carried out in order to gain more control on the construction of heterogeneous catalysts active sites. In this context, an organometallic chemistry approach can become important with particular attention paid to the interaction between the support and organometallic precursors [2]. By using functions that are already present on the support, or by grafting first suitable ligands on its surface, organometallic complexes could react selectively with these groups, leading to a uniform and controlled distribution of active species on the support [2,3]. This strategy has been applied to active carbon as support by building suitable surface functions [4-10]. The presence of carboxylate groups in particular on the carbon surface allowed the incorporation of functions playing the role of ligands for organometallic complexes by derivatization.

E-mail address: Sophie.Hermans@uclouvain.be (S. Hermans).

ABSTRACT

Molecular phosphine–carbonyl palladium clusters were anchored onto a phosphine-functionalized carbon support (C_{PPh2}) by ligand exchange. This support was characterized by solid-state NMR prior to reaction with the clusters. The same clusters were also deposited on the non-functionalized support (C_{SX+}). Characterization by SEM and XPS showed that the surface was more uniform when using the functionalized support. After thermal activation, the Pd/C materials obtained were characterized by CO chemisorption, XPS, SEM, TEM, powder XRD and analyzed for metal loading by ICP-OES. Again, the solids prepared with the functionalized support presented a more uniform surface. TEM indicated that small nanoparticles (1–10 nm) were present on the surface with narrow size distributions. The activated Pd/C materials proved to be efficient catalysts for the hydrogenation of nitrobenzene into aniline. They were competitive with commercial and literature catalysts. Moreover, the catalysts prepared using the functionalized support were more active and more stable than when using C_{SX+} .

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In heterogeneous catalysis, the use of transition metal clusters as precursors is also interesting due to their high potential to control (i) the size of the obtained supported particles via their nuclearity and (ii) the chemical composition of these particles via their stoichiometry [11]. Moreover, they generally lead to a better dispersion than mononuclear complexes [11]. For instance, clusters have been used as precursors on oxide supports for hydrogenation reactions [3,12–17]. They were mostly deposited on the intact support without particular pretreatment, but sometimes the occurrence of covalent interactions with the support was reported. Clusters have also already been incorporated on carbon [18-22] but without specific interactions. Nevertheless, to obtain active catalysts, the supported clusters have to be activated to remove the ligand shell and to obtain supported metallic particles. This decarbonylation step, as most of the clusters used as precursors are carbonyl clusters, is known to lead to agglomeration and fragmentation of the supported clusters [12]. To avoid losing the advantage of using clusters as precursors and to obtain a high dispersion of these entities on a carbonaceous support even after activation, it would be useful to incorporate on a carbon surface suitable functions that may act as anchoring ligands for clusters.

The hydrogenation of nitro-compounds is of interest for a range of applications, as amines are used as basic raw materials for polyurethanes, rubber chemicals, dyes or pharmaceutical compounds for example [23]. In particular, the hydrogenation of nitrobenzene (NB) into aniline (AN) (Scheme 1) has been well studied [24–27]. The catalysts usually efficient for this reaction are

^{*} Corresponding author. Tel.: +32 10 47 28 10; fax: +32 10 47 23 30.

¹ Present address: University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, United Kingdom.

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Scheme 1. Hydrogenation of nitrobenzene (NB) into aniline (AN).

based on noble metal (mainly Pd) supported on carbon. In this case, the two intermediates are not quantifiable because they are too reactive and do not accumulate. The structure–sensitivity of this reaction is well-known [25], with reaction rates depending both on dispersion and structure of metallic particles. Hence it is an ideal reaction to unravel structure–activity relationships.

In this work, we report the synthesis of Pd/C catalysts from heteroleptic carbonyl-phosphine palladium clusters. In order to benefit from the advantage of using clusters as precursors, we used a functionalized carbon support [28], which comprises chelating phosphine groups on its surface (Scheme 2). These were linked to carboxyl groups introduced by HNO₃ oxidation via ethylenediamine which was derivatized by double phosphinomethylation. These groups allow anchoring of clusters on the support through covalent bonds, and this is assumed to prevent, or at least to limit, agglomeration of the incorporated clusters and to keep them well-dispersed after activation [29]. Indeed, carbonyl clusters are known to exchange easily one or more ligands for chelating phosphines [30]. Here, we describe first the anchoring of the complex $[Pd(dba)_2]$ (1) and of the clusters $[Pd_{10}(CO)_{12}(PBu_3)_6]$ (2), $[Pd_{12}(CO)_{17}(PBu_3)_5]$ (3), $[Pd_4(CO)_5(PPh_3)_4]$ (4), $[Pd_{10}(CO)_{12}(PPh_3)_6]$ (5) and $[Pd_{24}(CO)_{32}(PPh_3)_3]$ (6). All these precursors were anchored on the functionalized support (C_{PPh2}) by ligand exchange and incorporated by non-specific interactions on the unmodified carbon (C_{SX+}) for comparison. We define anchoring as the covalent linkage of a metallic complex (here a cluster) via an organic tether covalently bound to the surface. Then, these supported clusters were thermally activated to give Pd/C catalysts, which were tested in the hydrogenation of nitrobenzene into aniline as a test-reaction for structure effects.

2. Materials and methods

2.1. Materials

All manipulations for the preparation of the catalysts were carried out under oxygen-free nitrogen or carbon monoxide atmosphere using Schlenk techniques and the samples were stored under Ar. All solvents used for these preparations were dried and distilled before use. The starting active carbon SXplus (noted SX+, acid-washed steam activated carbon, ash content: 6%; $S_{\text{BET}} = 922 \text{ m}^2/\text{g}; S_{\text{B}\text{I}\text{H}} = 245 \text{ m}^2/\text{g}; \text{ pore volume [BJH]} = 0.41 \text{ cm}^3/\text{g})$ was supplied by NORIT, sieved to keep only the fraction of granulometry 50–100 μ m and noted C_{SX+}. The complex [Pd(dba)₂] (**1**) was purchased from Aldrich and used as received. The 5 wt.% commercial Pd on charcoal catalyst (type 58 paste, 49.6% H₂O, Johnson Matthey, noted [M_{5%}) was purchased from Johnson Matthey and dried before use. The functionalized carbon support (noted C_{PPh2}) and the clusters $[Pd_4(CO)_5(PPh_3)_4]$ (4), $[Pd_{10}(CO)_{12}(PPh_3)_6]$ (5) and $[Pd_{24}(CO)_{32}(PPh_3)_3]$ (6) were prepared as previously described by us [28,29,31]. The clusters $[Pd_{10}(CO)_{12}(PBu_3)_6](2)$ and $[Pd_{12}(CO)_{17}(PBu_3)_5]$ (3) were prepared as described by Mednikov et al. [32,33].

2.2. Catalysts preparation

Two types of catalysts were prepared: (i) clusters anchored on C_{PPh2}, and (ii) clusters deposited on C_{SX+}. The amount of cluster engaged in each anchoring experiment corresponded to a theoretical 3 wt.% metal loading on the support after removal of the ligands. The experimental conditions for incorporation of the different precursors on the supports are summarized in Table 1. In a typical experiment, the appropriate quantity of cluster was introduced with 582 mg of support and 40 mL of solvent or mixture of solvent (20 mL/20 mL) in a round bottom Schlenk flask. Then, the suspension was stirred at room temperature for 5 days in the dark under nitrogen (or carbon monoxide for clusters **4–6**). The suspension was filtrated and the isolated solid was washed with the used solvents and dried at room temperature under vacuum. In order to determine the amount of incorporated cluster on the support, the filtrate was kept for further analysis by palladium atomic absorption using a PERKIN ELMER 3110 spectrometer fitted with a flame atomizer.

To obtain the desired activated catalysts, the supported clusters were submitted to a thermal treatment in a tubular oven STF 16/450 from CARBOLITE. The samples were placed into porcelain combustion boats and heated at $300 \,^\circ$ C for 1 h for the clusters and at $400 \,^\circ$ C for 1 h for [Pd(dba)₂] (heating ramp: $100 \,^\circ$ C/h) under a N₂ stream. These activation conditions were obtained by thermal studies of the clusters in their pure form, by TGA analyses on a TGA SDTA 851e instrument from METTLER TOLEDO. These analyses were carried out with a heating ramp of $10 \,^\circ$ C/min and under N₂ flow (100 mL/min) and the samples (~3 mg) were placed into alumina containers (70 µL).

Two references samples for solid-state NMR studies were prepared under nitrogen as follows. First, HOCH₂PPh₂ was prepared by mixing 1.08 mL HPPh₂ (6.24 mmol) with 157 mg CH₂O (5.23 mmol) in 6 mL methanol, and heating 10 min at 70 °C. This mixture was added to 600 mg C_{SX+} and stirred at room temperature for 30 min before evaporating the solvent under reduced pressure. Second, 1.08 mL HPPh₂ (6.24 mmol) were added to 600 mg of C_{SX+} in 10 mL toluene, before stirring at room temperature for 30 min and evaporating the solvent under reduced pressure as well.

2.3. Characterization

XPS (X-ray Photoelectron Spectroscopy) analyses were carried out at room temperature on a SSI-X-probe (SSX-100/206) photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocus Al X-ray source. Samples were stuck on small troughs with double-face adhesive tape and then placed on an insulating home-made ceramic carousel (Macor[®],Switzerland). Charge effects were avoided by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale was calibrated with reference to the peak Au4f_{7/2} at 84 eV, and the binding energies were calculated with respect to the <u>C</u>–C, H) component of the C 1s peak fixed at 284.8 eV. Data treatment was performed with the CasaXPS program (Casa



Scheme 2. Support functionalization.

Software Ltd., UK). The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

SEM images were acquired on a FEG digital scanning microscope (DSM 982 Gemini from LEO) equipped with a EDXS detector (Phoenix CDU LEAP). The samples were fixed by double-sided conducting adhesive tape onto aluminum specimen stubs from Agar Scientific.

TEM images were obtained with a LEO 922 OMEGA energy filter transmission electron microscope. The samples were suspended in hexane under ultrasonic treatment, then allowed to settle to discard the biggest particles. A drop of the supernatant was then deposited on a holey carbon film supported on a copper grid, which was dried overnight under vacuum at room temperature, before introduction in the microscope.

The X-ray diffraction (XRD) analyses were recorded on a SIEMENS D5000 diffractometer equipped with a copper source ($\lambda_{K\alpha}$ = 154.18 pm). The samples were placed on quartz monocrystals and the crystalline phases were identified by reference to the JCPDS-ICDD database.

Metal dispersion measurements were realized by CO chemisorption on a PulseChemisorb 2700 from MICROMERIT-ICS. The sample (about 30 mg) was first reduced under hydrogen flow (25 mL/min) at 150 °C for 1 h, then swept by a helium flow (25 mL/min) at 200 °C for 2 h. The sample was finally brought back to room temperature, at which point it was subjected to a sequence of CO pulses. The metal dispersion was calculated from the cumulative amount of adsorbed CO (i.e., the sum of nondetected CO in each pulse), following $D = (V_{\text{NTP}} \cdot M/V_{\text{M}} \cdot m \cdot C \cdot P) \times 100$, where *D* is the

Table 1

Incorporation of the different precursors on the supports C_{SX^+} and C_{PPh2} .

metal 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 under 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), and *P* is the wt.% of metal in the sample.

Solid-state NMR experiments were conducted at 9.4T using a Bruker Avance DSX400 spectrometer equipped with a ${}^{1}H/{}^{19}F/X$ 2.5 mm probe. Samples were spun in zirconia rotors of 2.5 mm outer diameter. ${}^{31}P{}^{1}H{}$ MAS NMR spectra were acquired at 161 MHz and 400.16 MHz for ${}^{31}P$ and ${}^{1}H$, respectively, at a MAS rate of 10 kHz. A ${}^{31}P\pi/3$ pulse of 1.9 μ s was used for excitation whilst TPPM decoupling was used during acquisition with a recycle delay of 120 s. Chemical shifts are quoted in ppm relative to 85 wt.% H₃PO₄ solution.

Pd content of the obtained catalysts was determined by ICP-OES elemental analyses carried out by Medac Ltd. after dissolution of the samples by acid digestion.

2.4. Catalytic hydrogenation of nitrobenzene (NB) into aniline (AN)

The catalytic tests were carried out in a steel Parr 4521 reactor fitted with a temperature control device and a mechanical stirrer fixed at 2500 rpm. First, 350 mL of methanol (Fluka, p.a., >99.8%), a precisely weighted out amount (\sim 0.075 g) of catalyst and of 1-butanol as chromatographic internal standard (\sim 2.9 g \approx 3.66 mL;

Precursor	Amount of precursor	Support	Solvents ^a	Yield (%) ^b	Loading (wt.%) ^c	XPS Pd/C _{exp}	XPS Pd/C_{calc}^{d}
$[Pd(dba)_2](1)$	97.2 mg	C _{SX+}	DCM/Tol	99.9	3.0	0.020	0.003
	97.2 mg	C _{PPh2}	DCM/Tol	69.9	2.1	0.022	0.002
$[Pd_{10}(CO)_{12}(PBu_3)_6](2)$	44.2 mg	C _{SX+}	Hex	82.3	2.5	0.007	0.003
	44.2 mg	C _{PPh2}	Hex	50.7	1.5	0.017	0.002
$[Pd_{12}(CO)_{17}(PBu_3)_5](3)$	38.9 mg	C _{SX+}	Hex	85.6	2.6	0.010	0.003
	38.9 mg	C _{PPh2}	Hex	84.3	2.5	0.022	0.003
$[Pd_4(CO)_5(PPh_3)_4](4)$	76.2 mg	C _{SX+}	THF	32.3	1.0	0.011	0.001
	76.2 mg	C _{PPh2}	THF	45.2	1.4	0.010	0.002
$[Pd_{10}(CO)_{12}(PPh_3)_6](5)$	50.4 mg	C _{SX+}	THF/Tol	71.4	2.2	0.029	0.002
	50.4 mg	C _{PPh2}	THF/Tol	58.9	1.8	0.014	0.002
$[Pd_{24}(CO)_{32}(PPh_3)_3]$ (6)	28.8 mg	C _{SX+}	DCM	94.7	2.8	0.017	0.003
	28.8 mg	C _{PPh2}	DCM	87.9	2.6	0.027	0.003

^a THF = tetrahydrofurane; Tol = toluene; DCM = dichloromethane; Hex = hexane.

^b The yield has been calculated by subtracting the amount of Pd detected in the filtrates from the amount of Pd engaged and by dividing this result by the amount of engaged Pd.

 c The metal loading has been calculated on the basis of the corresponding yield, considering 3 wt.% = 100% yield.

^d Calculated Pd/C values are bulk molar ratios and are dependent on the metal loading. The amount of Pd taken into consideration for the calculations corresponds to the amount of Pd actually anchored. The amount of C taken into consideration corresponds to the amount of support used, considering that it is only constituted of carbon, plus the carbonaceous contribution of the ligands (dba, PBu₃ or PPh₃).

Sigma-Aldrich, p.a., 99.8%) were poured into the reactor and degassed for 15 min under nitrogen. The mixture was then submitted to a pre-treatment at 80°C for 1h, under 15-20 bars of H₂. During this time, a precisely weighted out amount of reactant $(\sim 7.3 \text{ g} \approx 6.13 \text{ mL of nitrobenzene}; \text{ Janssen Chimica, 99\%})$ was dissolved in 19 mL of methanol and degassed (under N₂) for 10 min together with 25 mL of methanol. The temperature in the reactor was then fixed at 60°C and the pressure was lowered to 2–2.5 bars. The degassed nitrobenzene (NB) solution was added to the reactor mixture followed by the degassed methanol. Immediately, 5 bars of H₂ were added, which initiated the reaction. During catalytic reaction, the reactor was kept under a pressure of about 7-7.5 bars H₂. Sampling of the reaction mixture took place at regular time intervals, and the product distribution was obtained by gas chromatography. The chromatograph was an Agilent Technologies 6890 N fitted with a WCOT fused silica Chrompack CP-WAX 52 CB capillary column (length, 50 m; internal diameter, 0.53 mm; film thickness, 2 µm). The vector gas was He (50 kPa), and the temperature of the injector and detector was maintained at 250 °C. The samples were automatically injected via a split-splitless injector. The temperature program for analysis was as follows: start at 160 °C, heating to 240 °C (10 °C/min), 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 surface 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 by either the rate of nitrobenzene (NB) conversion or the rate of aniline (AN) formation. In this study, the catalysts are compared on the basis of the former. The conversion rate is calculated from the slope of the linear part of the evolution with time. Standard tests have been performed to ensure kinetic regime and to avoid diffusional limitations.

3. Results and discussion

3.1. Incorporation of clusters on the supports

The different clusters $[Pd_{10}(CO)_{12}(PBu_3)_6]$ (**2**), $[Pd_{12}(CO)_{17}(PBu_3)_5]$ (**3**), $[Pd_4(CO)_5(PPh_3)_4]$ (**4**), $[Pd_{10}(CO)_{12}(PPh_3)_6]$ (**5**) and $[Pd_{24}(CO)_{32}(PPh_3)_3]$ (**6**), used as precursors for the synthesized Pd/C catalysts, were prepared from literature procedures [31–33]. Their color and IR bands guarantee their unambiguous identification. The spectra recorded in this study gave C–O bond stretching bands between 2200 and 1600 cm⁻¹ that fit perfectly with literature data and confirmed the success of the syntheses.

The functionalized carbon support C_{PPh2}, prepared as previously described by us [28,29], was designed to anchor molecular clusters on its surface. Indeed, chelating phosphine groups were incorporated on its surface to act as ligands for noble metal molecular clusters. Within the framework of the present study, this solid product has been characterized by solid-state NMR prior to cluster incorporation. Fig. 1a and b displays the reference spectra and Fig. 1c is the spectrum obtained for C_{PPh2}. During the functionalization procedure, HPPh₂ is used as starting material, then transformed into the HOCH₂PPh₂ alcohol to be finally grafted as chelating phosphines on the support by derivatization of pending amines introduced beforehand. Reference spectra were taken for HPPh₂ (commercial) and the HOCH₂PPh₂ alcohol (prepared as described in [29] and used as such without purification) brought in contact with C_{SX+} for comparison (see Section 2). As expected, the spectrum of HPPh2 adsorbed on CSX+ gives only one single narrow band at 28.8 ppm (Fig. 1b), as there could be only one P-containing species. The material obtained from the HOCH₂PPh₂ alcohol leads to several bands in the NMR spectrum (Fig. 1a), which could arise either from by-products of the reaction of formation of this alcohol



Fig. 1. ³¹P{¹H} MAS NMR spectra of (a) HOCH₂PPh₂ deposited on C_{SX+} (b) HPPh₂ deposited on C_{SX+} and (c) C_{PPh_2} . Asterisks denote spinning sidebands.

and unreacted HPPh₂ (at 28.9 ppm) or from reactions between the alcohol and surface O-containing groups known to be present on the SX+ carbon. Finally, a very broad band is observed for the C_{PPh2} support (Fig. 1c), which is centered on a value different from both references described above. The width of the band arises from a broad distribution of chemical shifts indicating multiple chemical environments of the P-ligand in the phosphine-functionalized support. This was to be expected, as the double phosphinomethylation reaction is always accompanied by the single phosphinomethylation as secondary reaction, together with the fact that by-products cannot be washed out from the solid surface if covalently bound. However, the presence of sites with ³¹P chemical shifts different from the initial compounds indicates that a reaction did occur, forming some chelating groups on the surface of C_{PPh2}. Model studies in solution [29] have shown that the reaction path envisaged here does lead to a major yield in the desired chelating P-ligand, and that it is indeed able to react with organometallic cluster compounds in a non negligible way.

The different Pd precursors were incorporated on both supports C_{SX+} and C_{PPh2} (Table 1), in engaged amounts corresponding to a theoretical 3 wt.% metal loading. The obtained solids were analyzed by XPS (Table 1) and SEM. First, one can observe that the amount of Pd incorporated was higher in the case of the C_{SX+} support (excepted for 4), indicating its highly adsorbent properties. Secondly, the amount of Pd incorporated (loading) was in general higher than 2 wt.%. Cluster 4 presented the lowest yields of incorporation by opposition to **1** and **6** that presented the best yields. Thirdly, the XPS analyses indicated that the experimental Pd/C ratios were higher than the calculated ones. This seemed to indicate that the precursors are well-dispersed on the supports surface, at least on the external surface. In addition, one could observe that the Pd/C ratios were generally higher in the case of C_{PPh2} than C_{SX+} (except for 4 and 5) even though the absolute amount of incorporated Pd was lower. This seemed to indicate that the dispersion of the clusters is better on C_{PPh2} than on C_{SX+}, and that Pd remains more on the external surface (rather than within the pores) in the case of CPPh2. The dispersion difference was confirmed by SEM analyses. Indeed, even if the use of clusters as precursors permitted to obtain small particles (<50 nm) in all cases (C_{SX+} and C_{PPh2}), the registered SEM images showed that the obtained surface on C_{SX+} was less uniform than the one observed on C_{PPh2}: agglomerates (50-200 nm) were identified at the surface of C_{SX+} (Fig. 2).



Fig. 2. Representative SEM images of clusters incorporated on non-functionalized support C_{SX+} (before thermal treatment): (a) $[Pd_{10}(CO)_{12}(PBu_3)_6]$, (b) $[Pd_4(CO)_5(PPh_3)_4]$, (c) $[Pd_{10}(CO)_{12}(PPh_3)_6]$, and (d) $[Pd_{24}(CO)_{32}(PPh_3)_6]$.

These results show that the use of a functionalized support for the anchoring of molecular clusters helps to obtain more evenly dispersed nanoparticles [11]. The advantage of using clusters is to allow a ligand exchange process for anchoring onto the functionalized surface, and to offer nanoscopic building blocks for the final catalyst.

3.2. Activation and characterization of the catalysts

These supported clusters were then thermally treated in order to prepare supported Pd nanoparticles by removing the ligand shells. The experimental conditions were determined by TGA analyses of the precursors in their pure form (Table 2). All the clusters lose most of their ligands below 300 °C. Thus, the supported clusters were activated at 300 °C for 1 h under N₂. In the case of the complex $[Pd(dba)_2](1)$, the final decomposition temperature being at 400 °C, it implied an activation at this temperature for 1 h under N₂. However, in all cases, the experimental weight losses were lower than the calculated losses based on the assumption that all ligands would be removed. We believe that decarbonylation occurs more easily than removal of the phosphine ligands. Some remaining fragments belonging to the phosphine groups must therefore still be present after thermal treatment. In the case of the clusters anchored onto the phosphine-functionalized support, the situation might even be worse, as the phosphines are stabilized through covalent bond with the surface. This has been verified by XPS which shows the presence of P on C_{PPh2} after thermal treatment at 300 $^\circ C$ for 1 h under nitrogen.

The activated samples were first analyzed by elemental analysis, XPS and CO chemisorption. These results are displayed in Table 3. The exact metal loading of the Pd/C catalysts were determined by ICP-OES elemental analysis after dissolution. The numbers obtained correspond closely to the loading determined before activation by atomic absorption, meaning that the soft activation conditions used here to remove the clusters ligand shells did not cause loss of metal by volatilization. Catalysts **a**, **b**, **c**, **e**, **k** and **l** presented the highest loading with values between 2.4 and 3 wt.%. The catalyst **g** presented the lowest loading with 1 wt.% and all others presented a loading of around 2 wt.%. The obtained XPS Pd/C atomic surface

ratios after activation were generally similar to those before activation but slightly smaller. This decrease of the Pd/C ratios seems to indicate that some agglomeration occurred during the activation step. As before activation, the Pd/C ratios were generally higher for the catalysts supported on C_{PPh2}, indicating a better dispersion on the external surface of the functionalized support. The metal dispersion after activation was determined by CO chemisorption. The lowest values (3%) were observed for **a** and **b**, i.e. when starting from a mononuclear complex and the highest (>20%) for **c**, **e** and k. These results confirm the advantage of using clusters as precursors as they generally permit to obtain a better dispersion than with mononuclear precursors [11]. Surprisingly, when using clusters **2**, **3** and **6** as precursors, the dispersion was better on C_{SX^+} than on C_{PPh2}, while the opposite was found with **4** and **5**. This might indicate that, in the former cases, the ligand-exchange reaction on the functionalized support did not occur as well as with the latter. The values of Pd/C ratios measured by XPS displayed the opposite trend than the dispersion values (i.e. when Pd/C ratios measured by XPS decreased, dispersion increased, mainly for C_{SX+}-supported samples; the opposite being true for most CPPh2-supported samples). This confirms that Pd is more located on the external surface in the case of C_{PPh2}, causing lower dispersion. In the case of C_{SX+}supported samples, the metal penetrates deeper within the porous network, hence leading to higher dispersion.

The activated catalysts were also analyzed by XRD, SEM and TEM. The XRD diffractograms generally displayed no signal, indicating that the supported Pd particles were of very small sizes. Only catalysts **a**, **g** and **i** gave small peaks, indicating that these catalysts present the biggest particles on their surface. This is roughly in agreement with the CO chemisorption measurements (Table 3) as these catalysts were among those presenting the lowest dispersions. The recorded SEM images of the Pd/C catalysts did not bring any more information than before activation. The catalysts supported on C_{PPh2} presented generally a more uniform surface with small particles of similar sizes. In order to gain a more precise idea of the particles sizes, the catalysts supported on C_{PPh2} were characterized by TEM. The recorded images are displayed in Fig. 3 with an indication of the observed particle size. One can observe that the supported particles were of nanometrical sizes

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Fig. 3. TEM images of the activated Pd/C catalysts supported on C_{PPh2}.

(<10 nm) and evenly dispersed on the functionalized support C_{PPh2} . The catalysts **d**, **f** and **j** displayed the smallest particles (1–2 nm) amongst the C_{PPh2} -supported catalysts, with narrow sizes distributions. Catalysts **b** and **h** displayed bigger particles (1–5 nm), which is in agreement with CO chemisorption and XRD analyses, and **I** displayed the least uniform surface with particle sizes from 1 nm to 10 nm. These results confirm that the use of a functionalized support allows to obtain small and well-dispersed supported

Table 2Thermogravimetric analyses.

Precursor	Weight loss (%)	Final decomposition temp. (°C)	Calcd. weight loss (%)
1	72.5	400	81.5 (2 dba)
2	54.0	200	59.3 (12 CO + 6 PBu ₃)
3	47.4	200	$54(17 \text{ CO} + 5 \text{ PBu}_3)$
4	64.9	280	$76(5 \text{ CO} + 4 \text{ PPh}_3 + 2 \text{ CH}_2\text{Cl}_2)$
5	53.1	300	$64.2(12 \text{ CO} + 6 \text{ PPh}_3)$
6	24.4	250	39.7 (32 CO + 3 PPh ₃)

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Table J				
Characterization of	of the activated	Pd/C catalysts	and catalytic	result

Precursor	Name of obtained catalyst	Loading before activation (wt.%) ^a	Loading after activation (wt.%) ^b	XPS Pd/C ratios before activation	XPS Pd/C ratios after activation	Dispersion (%) ^c	Activity per g of catalyst (mol L ⁻¹ min ⁻¹ g ⁻¹)	TOF ^d
1	$Pd/C_{SX+}(\mathbf{a})$	2.99	2.97	0.012	0.014	3.0	0.0030	143
	Pd/C_{PPh2} (b)	2.11	2.44	0.022	0.015	3.0	0.0048	279
2	$Pd_{10Med}/C_{SX+}(\mathbf{c})$	2.48	2.35	0.007	0.006	29.1	0.0334	208
	Pd_{10Med}/C_{PPh2} (d)	1.54	1.68	0.017	0.012	17.4	0.0115	167
3	$Pd_{12Med}/C_{SX+}(\mathbf{e})$	2.58	2.78	0.010	0.008	25.6	0.0314	188
	Pd_{12Med}/C_{PPh2} (f)	2.54	2.11	0.022	0.016	7.8	0.0133	344
4	$Pd_4/C_{SX+}(\mathbf{g})$	0.99	1.02	0.011	0.006	3.3	0.0008	101
	Pd_4/C_{PPh2} (h)	1.38	1.81	0.010	0.006	8.1	0.0090	261
5	$Pd_{10}/C_{SX+}(i)$	2.16	1.94	0.029	0.014	7.4	0.0020	59
	Pd_{10}/C_{PPh2} (j)	1.79	1.98	0.014	0.010	12.3	0.0134	234
6	Pd_{24}/C_{SX+} (k)	2.85	2.61	0.017	0.014	22.1	0.0150	111
	Pd_{24}/C_{PPh2} (1)	2.65	2.93	0.027	0.021	9.1	0.0190	303
-	JM _{5%} ^e	-	5	n.d.	n.d.	11.8	0.0465	337

^a See Table 1.

^b The Pd loading after activation was determined by ICP-OES elemental analysis, except for JM_{5%} commercial catalyst.

^c Measured by CO chemisorption.

^d The TOF is expressed as the number of NB molecules reduced per surface Pd atom and per minute.

^e n.d. = non determined.



Fig. 4. Activity per g of Pd: catalysts supported on C_{SX+} in white and those supported on C_{PPh2} in black.

particles when using clusters as precursors. The catalyst prepared from mononuclear complex (**b**) and the catalyst prepared from the Pd_{24} compound (**l**), which is thought to be of colloidal nature [31], both display larger distributions of particle sizes. It should be noted however, that even in the case of clusters thought to be anchored on the phosphine-functionalized support, the final particle sizes do not correspond simply to the bare metallic core of the starting clusters. Some agglomeration still occurred, but to a lesser extent.

3.3. Nitrobenzene hydrogenation

All the catalysts prepared in this work and summarized in Table 3 were used in the hydrogenation of nitrobenzene into aniline as a standard test-reaction for structure effects. The resulting activity of each catalyst is also displayed in Table 3. For comparison, a commercial Pd 5 wt.%/C catalyst (JM_{5%}) was tested in the same conditions. Moreover, in order to verify that the pristine and functionalized supports do not play any role in the observed activity, as it can be the case with Pd/C catalysts used in nitroaliphatic compound (such as 2-methyl-2-nitropropane) hydrogenation [34], blank tests were conducted with the supports alone (without deposited metal). These experiments showed that the C_{SX+} support by itself does not give any conversion and that C_{PPh2} gives rise to a negligible activity of 0.0007 mol L⁻¹ min⁻¹ g⁻¹.

When looking at the activity per gram of catalyst (Table 3, second to last column), the JM_{5%} catalyst presented unsurprisingly the highest activity while Pd_4/C_{SX+} (g) presented the lowest one. This is due to their respective Pd loadings. As the loading varied among the different prepared catalysts, the activities have been normalized to be expressed per gram of Pd. These results are illustrated in Fig. 4. The highest activities were observed for Pd_{10Med}/C_{SX+} (**c**) and Pd_{12Med}/C_{SX+} (**e**) and not for the commercial catalyst anymore. These two catalysts presented the highest dispersions (see Table 3). The catalysts presenting the lowest activities (Pd/C_{SX+} (**a**), Pd/C_{PPh2} (**b**), Pd_4/C_{SX+} (**g**) and Pd_{10}/C_{SX+} (**i**)) were those with the lowest dispersions and showing signals in the X-ray diffractograms. The other catalysts presented activities comparable to $JM_{5\%}$ material. As shown in Fig. 5, the activity per gram of Pd is function of the



Fig. 5. Activity per g of Pd as a function of the dispersion (measured by CO chemisorption).



Fig. 6. Activity per g of accessible Pd: catalysts supported on C_{SX+} in white and those supported on C_{PPh2} in black.

dispersion. In this figure, plotting the activity per gram of Pd in function of the dispersion, a sequenced evolution is observed with a significant rise in activity when reaching 7–8% of dispersion and tending to a linear evolution above 20%. The evolution of the activity as function of dispersion is not regular, indicating that more subtle effects play a role in the activity differences observed.

Given this, the activities per gram of Pd were divided by the dispersion figures in order to obtain activities per gram of accessible Pd. In this way, the activities would represent the intrinsic performances of the surface Pd atoms playing a catalytic role. These results are displayed in Fig. 6. First, the activities are different for each catalyst, which confirms the "structure sensitive" nature of the reaction, as already mentioned in the literature [25]. Indeed, if the reaction was only dependent on the dispersion, all catalysts would present the same activity in Fig. 6. Secondly, the activities obtained for the catalysts supported on C_{PPh2} were generally higher (except for Pd_{10Med}/C) than those supported on C_{SX+} . Moreover, these activities were competitive with that of the commercial catalyst. This shows the advantage of using a functionalized support. The presence of a covalent link to a phosphine ligand probably alters the activation mechanism, retarding coalescence of metal atoms and crystallization of metallic phases. The obtained nanoparticles contain therefore more defects that are known to be very active sites. In addition, as XPS characterization unraveled, Pd is more situated on the external surface in the case of C_{PPh2}, making it more accessible for a liquid phase process. Indeed, internal diffusion of reactants within the pores of a microporous solid cannot be under-evaluated [35]. Moreover, we believe that, even if CO ligands are easily driven off by the activation procedure, some residue of the phosphine arm might remain underneath the metallic nanoparticles (see above comments in Table 2), acting as 'glue' with the support, but playing also electronic effects. It cannot be excluded either that some P atoms migrate within the nanoparticles.

Finally, for a better comparison with the results of the literature, TOFs, expressed as the number of NB molecules reduced per surface Pd atom and per minute, were also calculated (Table 3, last column). The catalysts obtained in our case presented activities similar to those described in the literature and prepared from H₂PdCl₄ [24]. No direct linear correlation between these activities and the dispersion had been observed either. However, it had been shown that when the dispersion decreases, the TOF increases, indicating that NB prefers plane catalytic sites than edges or corners [24,25]. This was also observed in our case, as the catalysts presenting the smallest particles in TEM images are not giving the highest TOFs values. On the contrary, the best TOF values are obtained for the catalysts **b**, **f** and **l** (Table 3, last column), which do not present particles smaller than 2 nm (see Fig. 3). It should also be noted that the TOF values are higher for catalysts supported on C_{PPh2} than on C_{SX+}, indicating again that the Pd atoms are somehow 'activated' by the preparation procedure involving a functionalized support.

The filtrates of the catalytic reaction media were analyzed by palladium atomic absorption in order to assess the metal losses of the catalysts during the tests. For example, catalyst **i** lost 82% of its metal content during catalytic test, while catalyst **j** retained all the palladium on its surface. Thus, functionalization of the support plays a significant role on the retention of the metallic phase during the catalytic tests. However, catalyst **l** presented a loss of 17% of Pd, indicating that all the metallic phase is not, each time, totally retained on C_{PPh2}, but that the loss is limited compared to the one observed on C_{SX+}. The residue of thermally-treated phosphines acting as 'glue' might explain this effect. Thus the major benefit of using a functionalized support resides in inhibition of metal leaching.

4. Conclusion

In this work, we have shown that molecular palladium clusters could be anchored onto a functionalized support in order to synthesize heterogeneous catalysts presenting well-dispersed supported nanoparticles. Five different carbonyl palladium clusters were incorporated on a phosphine-functionalized carbon support (C_{PPh2}) and on an unmodified one (C_{SX+}) for comparison. A mononuclear complex was also used as precursor as reference. The C_{PPh2} support was characterized by solid-state NMR in order to confirm the presence on its surface of covalently-grafted chelating phosphine groups. SEM images were recorded before and after thermal treatment and they showed that the surface of the functionalized support-derived samples was more uniform than with the unmodified C_{SX+}, i.e. presented less agglomerates. Surface Pd/C atomic ratios measured by XPS were generally higher on CPPh2 than on C_{SX+}. The size of the obtained activated particles on the functionalized support was confirmed by TEM and XRD analyses. TEM images showed well-dispersed particles with sizes comprised between 1 and 10 nm with a narrow size distribution (except for Pd_{24}/C_{PPh2}). The XRD patterns displayed most of the time no signal which confirms the formation of small particles. Metal dispersions were measured by CO chemisorption and were in agreement with the XRD measurements as the few catalysts presenting the lowest dispersions were those presenting small signals in the diffractograms. The lowest dispersions were obtained for $[Pd(dba)_2]$ on C_{PPh2} as well as on C_{SX+}, indicating that the use of clusters allows to obtain more efficiently well-dispersed particles than mononuclear complexes.

The Pd/C catalysts obtained displayed a catalytic activity in the hydrogenation of nitrobenzene into aniline. When the activities were normalized and expressed per gram of accessible Pd, the catalysts supported on C_{PPh2} presented a higher activity than

those supported on C_{SX+} . Moreover, they were competitive with a commercial catalyst and reports of the literature. These higher activities were ascribed to retarded formation of metallic nanoparticles during activation, enrichment in Pd on the external surface, and residual P from the tethering arm acting as glue. Additional catalytic tests showed that the use of a functionalized support permits to retain more efficiently the active phase at the surface of the catalysts during testing.

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