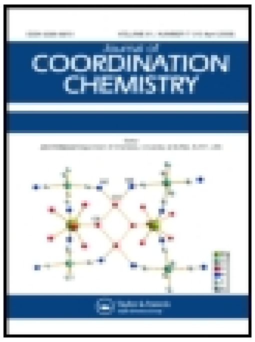

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Grafting and anchoring of molecular complexes as metal precursors for alumina-supported Pd catalysts

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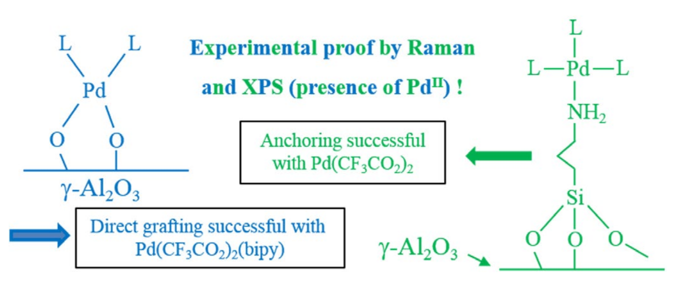
ABSTRACT

The surface coordination chemistry of Pd complexes on alumina has been studied in the framework of synthesizing Pd/γ-Al_2O_3 catalytic materials. Two methodologies were explored: the direct grafting of Pd complexes on hydroxyl functions present at the alumina surface and the anchoring of the precursors via amine-bearing silanes previously grafted on the support. Suitable conditions to graft and anchor Pd complexes on alumina surface were found and experimental proofs of grafting and anchoring processes are provided. The results show that covalent grafting indeed took place for samples prepared in acetonitrile with $[Pd(CF_3CO_2)_2(bipy)]$ and $[PdCl_2(PhCN)_2]$ complexes or with $[Pd(OAc)_2]$ and $[Pd(CF_3CO_2)_2]$ in acetone. The anchoring was successful for catalysts prepared in acetone with 1 wt.% of $[Pd(CF_3CO_2)_2]$ loading. Grafting and anchoring were found to stabilize palladium in its Pd(II) oxidation state. This has an adverse effect on the activation step that should lead to reduction of the complex to give the metallic catalytic supported active phase.



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1. Introduction

The majority of heterogeneous supported catalysts described in the literature are prepared by deposition of transition metals on oxide-type supports. The aim is to obtain high

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dispersion of the active phase on the support. However, most of the described processes used to bind the metal precursor onto the support are poorly defined. The following terms are used to describe the metal compound/support interactions: "supported," "adsorbed," "fixed," "immobilized," or "dispersed" [1–5]. These surface-immobilized molecular compounds are then usually reduced (or calcined) to produce supported metallic (or oxide) particles. In parallel, many studies about catalyst preparation in the literature report alternative methods such as grafting or anchoring, where a surface ligand exchange is targeted during metal precursor immobilization. This is usually carried out by appropriate choice of labile ligands in the starting metal compound, rather than using metal salts.

In this work, we will refer to definitions of grafting and anchoring as proposed by Lambert and Che [2]. Grafting is defined as the case where the native surface groups (usually hydroxyls) of the support are covalently bonded to a metal center and take part in its internal coordination sphere, thus acting as ligands. By opposition, 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 [2].

Given its widespread use as industrial catalytic support, we have chosen to focus here on alumina. Its surface chemistry, and in particular its surface coordination chemistry in the presence of soluble metal precursors has been far less studied than silica. However, some insight can be found in the existing literature. For example, an alumina supported Pd catalyst was prepared by sol-gel from [Pd(acac)$_2$] [6]. It was shown by FTIR, UV–Vis and ^{27}Al NMR that during aging of the gel a bond between Pd and Al precursor was created by ligand exchange. The reactivity of Pt(acac)$_2$ with Al_2O_3 pre-treated to give different hydroxylated surfaces was also studied by IR and UV–Vis spectroscopies. Only dehydroxylated alumina (by treatment at 350 °C) allowed surface reaction by ligand exchange to be observed [7]. By opposition, a study concerning the preparation of alumina-supported palladium catalysts describes a grafting methodology taking place at 117 °C in butanol [8]. At this stage, the catalyst was not characterized but it was calcined at 1000 °C to give PdO/Al_2O_3. The grafted precursor stage hence remains hypothetical.

Our aim is to explore the surface chemistry of soluble Pd complexes in interaction with gamma-alumina in order to be able to discriminate situations where a surface ligand exchange indeed took place from situations were a formal Pd-O-Al bond is not formed. This is studied with or without spacer, meaning by direct grafting of Pd complexes onto the hydroxyl functions of the alumina support or by anchoring of the precursor via organic arms previously grafted onto the support. By gathering experimental proof of the grafting or anchoring success, we wish to determine the appropriate conditions to favor these two processes. Model-compounds were selected for their ease of characterization using various spectroscopic methods. Support pretreatments and solvents were also varied, knowing their extremely important influence in this matter. Finally, the influence of the precursor state (grafted/anchored or not) on the final characteristics of the activated catalytic materials is evaluated.

2. Experimental

2.1. Materials

The support used is a gamma-alumina (γ-Al_2O_3) treated from its commercial form (Alfa-Aesar, 110 µm, 99.99%). The support was either dried at 150 °C under vacuum for 16 h (noted γ-Al_2O_3-d) or calcined in an oven at 550 °C under air for 16 h (noted γ-Al_2O_3-c).

The metallic precursors have been chosen in function of their grafting possibilities: palladium(II) acetylacetonate [$Pd(acac)_2$] (Aldrich 99%), bis(trifluoroacetato)(2,2′-bipyridine) palladium(II), [$Pd(CF_3CO_2)_2(bipy)$] (synthetized as described [9]), palladium(II) trifluoroacetate [$Pd(CF_3CO_2)_2$] (Aldrich 97%), dichlorobis(benzonitrile) palladium(II) [$PdCl_2(PhCN)_2$] (Aldrich 95%), and palladium(II) acetate [$Pd(OAc)_2$] (Rocc, Pd: 47.27%).

2.2. Direct grafting on the support surface

2.2.1. Mechanical mixture and wet impregnation (WI) for direct grafting

In a general procedure, 0.5 g of γ-Al_2O_3 were suspended with the metal precursor (amount corresponding to 5 wt.% Pd in final catalyst) in 25 mL of solvent. The mixture was ultrasonicated for 30 min. The suspension was stirred for 24 h at room temperature before being dried under vacuum in the case of the mechanical mixture and filtered for the wet impregnation case. The solid was analyzed by Raman spectroscopy and the filtrate (for WI) by atomic absorption spectrometry (AAS). The mechanical mixtures were carried out by stirring the support (γ-Al_2O_3-d or γ-Al_2O_3-c) with the precursor in a medium in which the precursor was not soluble, namely pentane (VWR, 99.7%). The wet impregnation method was realized by stirring the support and the precursor in a solvent in which the metal compound was soluble. All the prepared catalysts were activated in a tubular oven at 200 °C for 1 h under hydrogen. The activated catalysts were analyzed by XPS.

2.2.2. Wet impregnation under inert atmosphere

Some syntheses were carried out under oxygen-free argon using Schlenk techniques. 0.5 g of γ-Al_2O_3 (dried or calcined) was treated under vacuum overnight. Under inert atmosphere, the palladium precursor (amount corresponding to 5 wt.% Pd loading in final catalyst) was added together with 25 mL of solvent previously degassed. After 2 h reflux, the orange solution was filtered and the solid washed with 50 mL of solvent. The solid was analyzed by Raman spectroscopy and XPS. The filtrate was evaporated under vacuum and analyzed by Raman and re-dissolved in nitric acid to be analyzed by AAS. The prepared catalysts were reduced under hydrogen at 200 °C for 1 h in a tubular oven.

2.3. Solids prepared on functionalized γ-Al_2O_3 support by anchoring

2.3.1. Support functionalization

For anchored materials, a preliminary functionalization step [10–12] was realized in order to allow anchoring of the precursors on alumina. The γ-Al_2O_3 was dried at 100 °C under vacuum for 1 h followed by addition of one of the two selected silanes: 3-aminopropyltriethoxysilane (Acros Organics, 99%) which will give the support noted γ-Al_2O_3-1N (Figure 1) and N-[3-(trimethoxysilyl)propyl] ethylenediamine (Acros Organics, 97%) which gives the support noted γ-Al_2O_3-2N (Figure 2). In a typical experiment, 3 g of dried alumina (γ-Al_2O_3-d) was treated under vacuum for 30 min. Under inert atmosphere, 3.2 mL of aminopropyltriethoxysilane or of N-[3-(trimethoxysilyl)propyl] ethylenediamine and 50 mL of dried toluene were added. After 90 min stirring, a fraction of 10 mL (containing toluene and ethanol, produced by the reaction) was removed by distillation. Then, 1.6 mL of the corresponding silane and the amount of toluene corresponding to the amount removed earlier were added. The heating and distillation sequences were repeated twice before keeping the reflux overnight

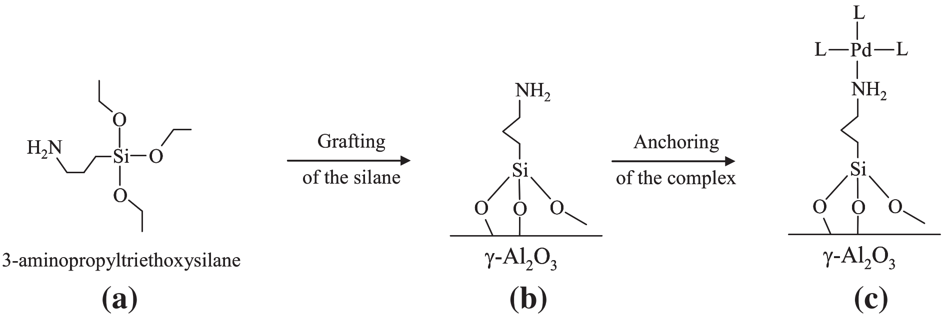


Figure 1. (a) Silane 1N, (b) Al_2O_3-1N, and (c) anchoring of Pd complex on functionalized alumina.

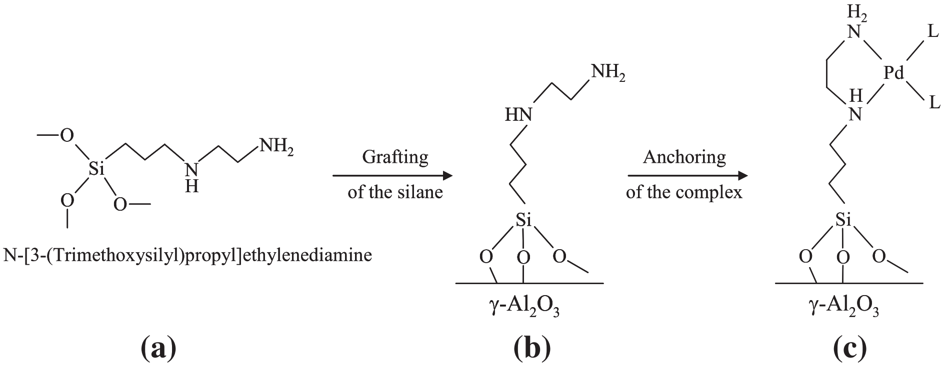


Figure 2. (a) Silane 2N, (b) Al_2O_3-2N, and (c) anchoring of Pd complex on functionalized alumina.

under inert atmosphere. The solid was filtered out and washed with 50 mL of dichloromethane, then further washed in a Soxhlet apparatus during 24 h (12 h with 180 mL of dichloromethane and then 12 h with 180 mL acetone).

2.3.2. *Anchoring on the functionalized support*

The anchoring reactions started from the functionalized supports γ-Al_2O_3-1N or γ-Al_2O_3-2N. Al_2O_3-d was also used as such to provide "blank" references. The solvents used are acetone (VWR, 99.9%) and ethanol (VWR 99.9%). In a typical experiment, 1 g of alumina was treated under vacuum for 30 min. Under inert atmosphere, a given amount of palladium precursor (corresponding to 5 wt. Pd % in the final catalyst) and 25 mL of solvent were added to the flask. After 4 h stirring at room temperature, the solution was filtered. The light yellow solid was washed with 50 mL of solvent and analyzed by Raman spectroscopy and XPS while the filtrate was analyzed by AAS. The prepared catalysts were reduced under hydrogen at 200 °C for 1 h in a tubular oven.

The samples prepared as described in the section "Mechanical mixture and wet impregnation" will be noted *G-(WI)-sample number*. Those prepared as described in the anchoring section will be noted *A-sample number_(ref/Si^{1N} or Si^{2N})* depending on whether they are prepared on unfunctionalized alumina or alumina functionalized with the silane-1N (Figure 1) or 2N (Figure 2). For the activated catalysts, the letter ***a*** in lower case will be added in the designation.

2.4. Characterization techniques

2.4.1. Raman spectroscopy

FT-Raman spectra were recorded on a Bruker spectrometer (type RFS100/S) equipped with a liquid nitrogen detector and a Nd:YAG laser supplying the excitation line at 1064 nm. Wavenumber calibration of the instrument was checked regularly using the S_8 peaks at 219 and 153 cm^{-1}. The spectral resolution is about 4 cm^{-1}.

2.4.2. Infrared spectroscopy

The infrared spectra were taken with a FT-IR Bruker spectrophotometer Equinox 55. The measurements were carried out with samples containing 1 wt.% of the sample in KBr pellets in transmission mode (analysis range: from 4000 to 400 cm^{-1}).

2.4.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on a SSI-X-probe (SSX-100/206) spectrometer from Fisons. The samples were pressed on little stainless steel cell-cups and then placed on an insulating home-made ceramic carousel with a nickel grid positioned 3 mm above the sample surface, to avoid differential charging effects: a floodgun set at 8 eV was used for charge stabilization. The C_{1s} binding energy of carbon (C-C,H) set at 284.8 eV was used as an internal standard value. Data treatment was performed with the CasaXPS program (Casa software Ltd). The analytical peaks used were C_{1s}, Pd_{3d}, Na_{1s}, Cl_{2p}, O_{1s}, N_{1s}, Al_{2p}, F_{1s}, and Si_{2s}. The following constraints were used for decomposition in the case of Pd: intensity ratios: $I(\text{Pd } 3d_{5/2})/I(\text{Pd } 3d_{3/2}) = 1.5$, FWHM ratio = 1, $\Delta(\text{Pd } 3d_{5/2}\text{-Pd } 3d_{3/2}) = 5.26$ eV.

2.4.4. Atomic absorption spectroscopy (AAS)

The quantification of Pd in the synthesis filtrates was performed by atomic absorption analysis using a Perkin-Elmer 3110 spectrometer equipped with an air-acetylene flame atomizer. The calibration curve (from 1 to 10 mg/L Pd) was realized with standard solutions obtained by dilution of a commercial palladium (1006 µg/mL, Acros) solution.

2.4.5. Thermogravimetric analysis

The thermal analyses were realized with a combined TGA-DSC analyzer (SDT 2960) from TA instruments, under nitrogen flow (100 mL min^{-1}), with a heating ramp of 10 °C min^{-1} (analysis range: 20–1100 °C). The samples were placed in alumina containers.

3. Results and discussion

The goal of the present study is to gather experimental proof confirming or refuting the hypothesis of a covalent grafting or anchoring of palladium complexes on gamma-alumina surface. For that purpose, a precise methodology was set up for both grafting and anchoring studies (Figure 3). Concerning grafting, the first step consisted in the treatment of alumina by drying under vacuum or calcination under air. The two treated alumina solids present different surface properties that have been studied and compared. The second step was the

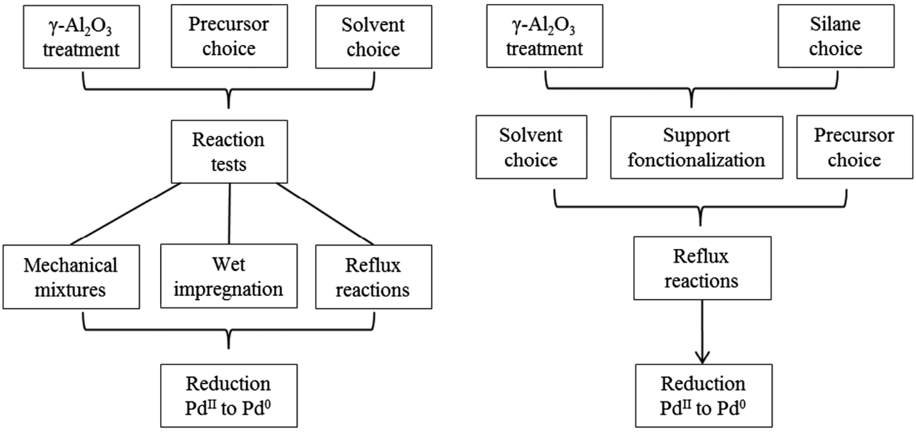


Figure 3. Methodology used for the grafting and anchoring studies.

choice of appropriate metallic precursors. These have been selected for their ease of undergoing ligand exchange reactions and/or their facility to be analyzed spectroscopically. Formal proof of grafting would be obtained if the Pd precursor exchanges one of its ligands for surface hydroxyls without changing its Pd(II) oxidation state. Solubility tests have been carried out to determine the most appropriate solvent for each precursor. Mechanical mixtures were prepared in a medium in which the precursor was not soluble, whereas wet impregnations were carried out in a solubilizing solvent. All samples obtained were analyzed by Raman spectroscopy. Finally, reactions were tested under reflux in order to push further the eventual grafting. Next to Raman spectroscopy, XPS was used to quantify the amount of Pd at the alumina surface and the presence of palladium in its Pd(II) oxidation state which would prove the grafting mechanism as defined in the introduction.

Concerning the anchoring study, the methodology was quite similar: the alumina was first treated by drying under vacuum and the most appropriate silanes permitting the anchoring of Pd complexes were selected (namely N-terminated ones). The support was functionalized by silane reaction with the surface hydroxyl groups. The precursors and solvents were then chosen for Pd anchoring on these functionalized supports. Reference reactions with the non-functionalized support have been tested in the same conditions in order to make comparisons. The solids were characterized by Raman and XPS and the filtrates by AAS to verify the anchoring success.

3.1. *Direct grafting on the alumina surface*

3.1.1. *Materials selection*

Two support pretreatments were carried out: drying under vacuum or calcination under air. The commercial support γ-Al_2O_3 has a highly hydrated surface under ambient conditions which could limit access of palladium complexes to the surface hydroxyl groups (Figure 4(b.1)). By opposition, when alumina is dried under vacuum at 150 °C for 16 h, it displays a surface without excess water molecules (Figure 4(b.2)) [13, 14]. When γ-alumina is calcined at 550 °C for 16 h, the support presents an even lower amount of hydroxyl functions, but more strained Al-O-Al bonds at the alumina surface (Figure 4(b.3)) which could give higher reactivity with

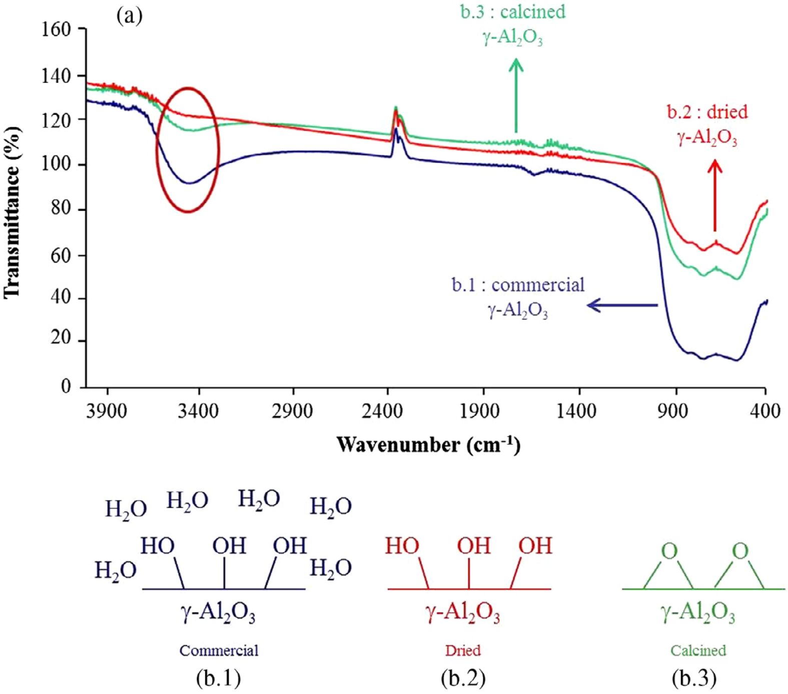


Figure 4. Comparison of the three alumina solids by infrared spectroscopy.

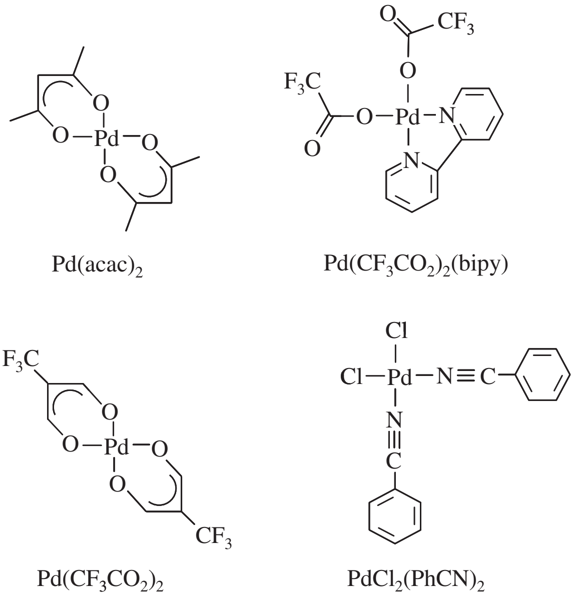
complex molecules. Figure 4(a) shows that the higher the heating temperature, the lower the number of hydroxyl groups (peak at 3400 cm^{-1}) on the surface. This might influence the grafting behavior.

Several palladium precursors were chosen (Figure 5), which exhibit specific fingerprints in their Raman spectra (S1). The precursor selection was based on their facility to exchange some of their ligands (*e.g.* carboxylates) and the easy quantification of atoms like fluorine by XPS to evaluate the efficiency of the exchange reactions. [Pd(acac)$_2$] was selected also because it is a common precursor for covalent grafting on alumina [7, 8].

Solubility tests (Table 1) were carried out to determine the most appropriate conditions for grafting these various precursors. Pentane was chosen for the synthesis as a non-solubilizing medium. For wet impregnations, toluene or acetonitrile were used for precursor solubility.

3.1.2. Mechanical mixtures

The precursor and the support were contacted in a medium in which the former was not soluble to obtain “blank” references for non-grafted species. The mechanical mixture obtained in the case of [Pd(acac)$_2$] for example was analyzed by Raman spectroscopy in order to compare it with spectra of the support or the precursor alone (Figure 6). The Raman spectrum of the mixture gives perfect overlapping of the two separate components proving that no grafting reaction occurred. The same observation could be made for [Pd(CF$_3$CO$_2$)$_2$(bipy)]. In the case of [Pd(CF$_3$CO$_2$)$_2$] and [PdCl$_2$(PhCN)$_2$] with the two treated alumina supports, decomposition of the precursor was observed. In the Raman spectra of these mechanical



$Pd(acac)_2$ $Pd(CF_3CO_2)_2(bipy)$

$Pd(CF_3CO_2)_2$ $PdCl_2(PhCN)_2$

Figure 5. Palladium precursors selected for the grafting study.

Table 1. Solvents used for each precursor based on solubility tests.

Precursor	Solubilizing medium	Non-solubilizing medium
$[Pd(acac)_2]$	Toluene	Pentane
$[Pd(CF_3CO_2)_2(bipy)]$	Acetonitrile	Pentane
$[Pd(CF_3CO_2)_2]$	Acetonitrile	Pentane
$[PdCl_2(PhCN)_2]$	Acetonitrile	Pentane

mixtures, the peaks corresponding to the precursor were not present anymore. In addition, a color change was observed.

3.1.3. Wet impregnation

Here, the precursor and the support were introduced in a solvent in which the precursor was soluble. Under these conditions, ligand exchange could occur between the precursor and the surface –OH groups. Several combinations were tested (Table 2). The results obtained for the two precursors $[Pd(acac)_2]$ and $[Pd(CF_3CO_2)_2(bipy)]$ did not show any proof of ligand exchange because the Raman spectra displayed, as for the mechanical mixtures, either the peaks of the intact precursor or precursor decomposition (see Figure S2 in Electronic Supplementary Material).

3.1.4. Wet impregnation under inert atmosphere and refluxing conditions

The syntheses under reflux in inert atmosphere were carried out in order to be in optimal conditions to allow covalent grafting by ligand exchange. A high temperature indeed favors kinetically the reaction efficiency; the inert atmosphere protects the reagents from decomposition.

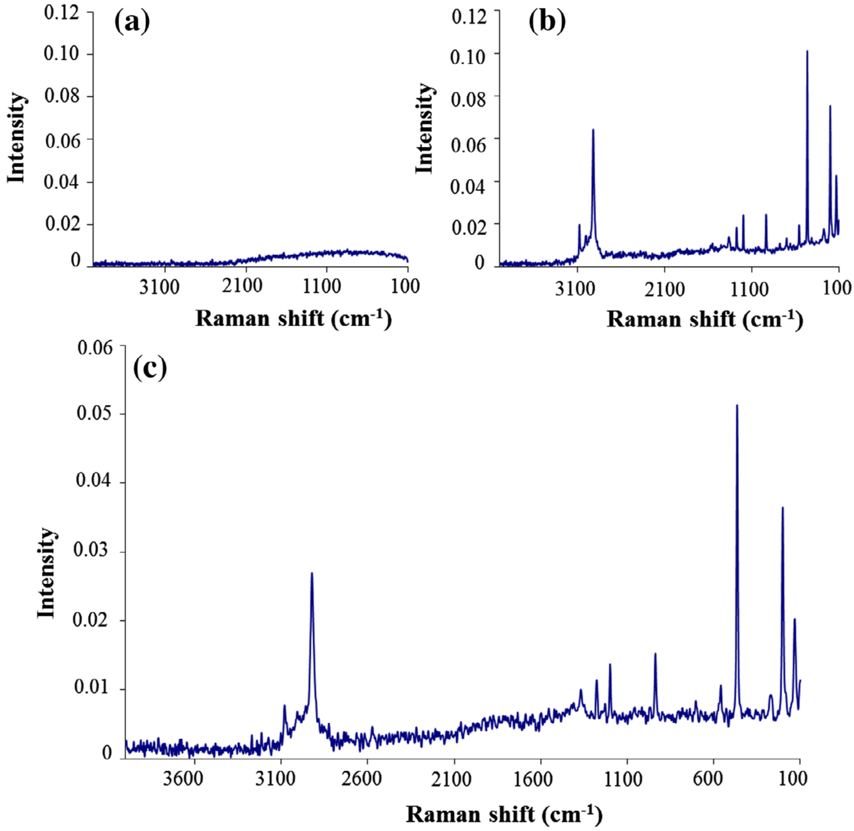


Figure 6. Raman spectra of (a) commercial γ-Al_2O_3, (b) [Pd(acac)$_2$], and (c) mechanical mixture [Pd(acac)$_2$]/γ-Al_2O_3.

Table 2. Wet impregnation syntheses: combinations tested.

Precursor	Support	Solvent	Exp. conditions	Work up
Pd(acac)$_2$	γ-Al_2O_3	Toluene	30 min ultrasound	Vacuum drying
Pd(acac)$_2$	γ-Al_2O_3	Toluene	30 min ultrasound + 24 h stirring	Vacuum drying
Pd(CF_3CO_2)$_2$(bipy)	γ-Al_2O_3	Acetonitrile	30 min ultrasound	Vacuum drying
Pd(CF_3CO_2)$_2$(bipy)	γ-Al_2O_3-c	Acetonitrile	Stirring 24 h	Filtration
Pd(CF_3CO_2)$_2$(bipy)	γ-Al_2O_3-d	Acetonitrile	Stirring 24 h	Filtration

3.1.4.1. Pd(acac)$_2$ in toluene. The solid samples and their filtrates after 24 h reaction were analyzed by Raman spectroscopy (Figure 7(a) and (b)). On the dried alumina (G-WI-1), the peaks in the Raman spectrum correspond to fluorescence due to the presence of palladium (Figure 7(a)). Fluorescence is observed here due to the particular Raman excitation line wavelength (1064 nm) selected, and can be used as a diagnosis for the presence of Pd in all cases. The precursor was partially decomposed during the synthesis but an intact part of it could be detected in the Raman spectrum of the filtrate. In the case of the solid G-WI-2 prepared with calcined alumina, no peak at all was observable for the solid (Figure 7(b)) meaning that most of the precursor remained in the filtrate as shown on Figure 7(d). XPS characterization of the solids showed the presence of Pd(0) in both cases and a very weak

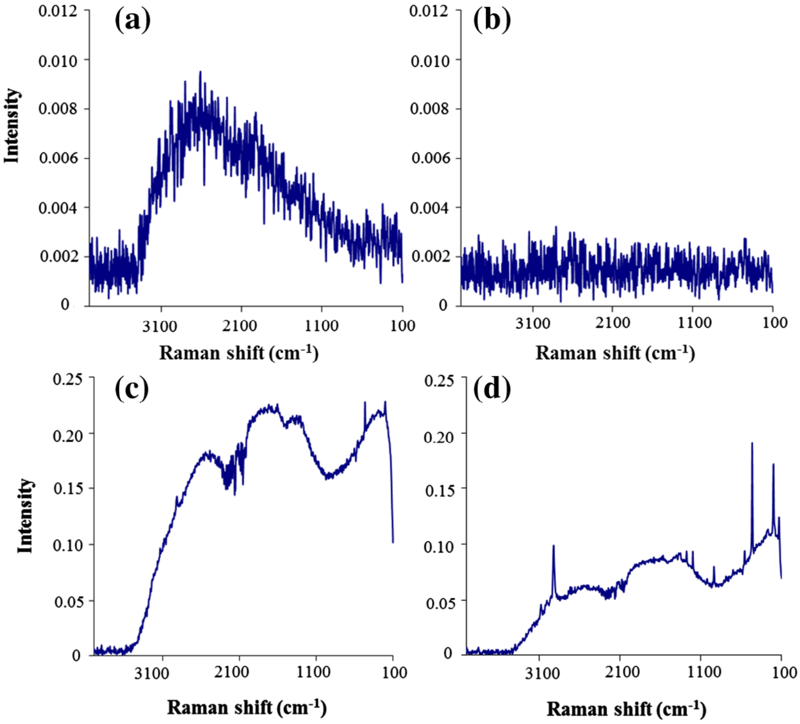


Figure 7. Raman spectra of (a) G-WI-1 solid, (b) G-WI-2 solid, (c) G-WI-1 filtrate, and (d) G-WI-2 filtrate.

Table 3. XPS results for the solids prepared in toluene from [Pd(acac)$_2$].

Code	Support	Reaction time	Pd/Al	% at. Pd	Pd^0/Pd^{II}
G-WI-1	γ-Al_2O_3-d	24 h	0.016	0.56	Pd^0
G-WI-2	γ-Al_2O_3-c	24 h	0.021	0.73	Pd^0
G-WI-3	γ-Al_2O_3-d	2 h	0.057	1.80	Pd^0 >>> Pd^{II}
G-WI-4	γ-Al_2O_3-c	2 h	0.014	0.48	Pd^0 ≈ Pd^{II}

atomic Pd % at the alumina surface confirming the partial decomposition of the precursor (Table 3). The duration was then reduced to 2 h and the results were similar: Pd(0) was present on both supports, and the majority of the precursor was retrieved in the filtrate. Nevertheless, for G-WI-3, prepared on dried alumina, a small proportion of Pd(II) was observed by XPS which could correspond to grafted palladium. For this reason, the subsequent reactions were heated for 2 h only.

3.1.4.2. *Syntheses in acetonitrile by grafting.*

The precursors [Pd(CF_3CO_2)$_2$], [Pd(CF_3CO_2)$_2$(bipy)] and [PdCl$_2$(PhCN)$_2$] have been tested on both treated aluminas in acetonitrile. For [Pd(CF_3CO_2)$_2$(bipy)], no fluorescence appeared on the Raman spectrum of the solid obtained after 2 h reaction under reflux meaning probably that no Pd(0) was formed. A large amount of precursor was found in the filtrate (Figure 8). However, the XPS results showed the presence of Pd(0) and Pd(II) for G-WI-5 and only Pd(II) for G-WI-6 which is ascribed to successful grafting of the precursor. The F/Pd ratio is weak for the latter suggesting the loss of at least one $CF_3CO_2^-$ ligand which confirms surface ligand exchange as expected (Table 4). For [Pd(CF_3CO_2)$_2$], Pd(0)

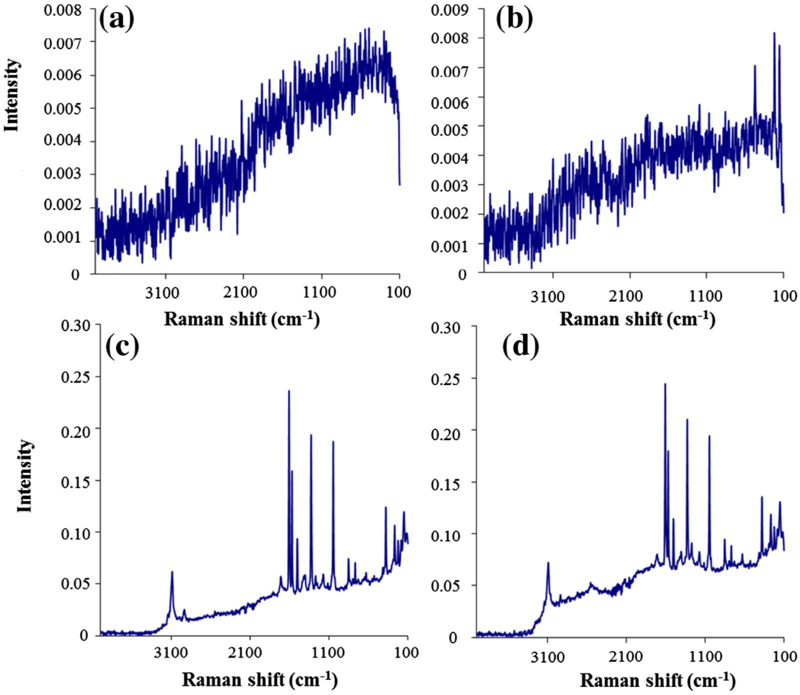


Figure 8. Raman spectra of (a) G-WI-5 solid, (b) G-WI-6 solid, (c) G-WI-5 filtrate, and (d) G-WI-6 filtrate.

Table 4. XPS results for the solids prepared in acetonitrile at 100 °C for 2 h.

Code	Precursor	Support	Pd/Al	F/Pd		% at. Pd	Pd^0/Pd^{II}
G-WI-5	$[Pd(CF_3CO_2)_2(bipy)]$	γ-Al_2O_3-c	0.005	12.4		0.16	$Pd^0 \approx Pd^{II}$
G-WI-6	$[Pd(CF_3CO_2)_2(bipy)]$	γ-Al_2O_3-d	0.051	2.22		1.60	Pd^{II}
G-WI-7	$[Pd(CF_3CO_2)_2]$	γ-Al_2O_3-d	0.153	0.64		4.74	$Pd^0 >>> Pd^{II}$
G-WI-8	$[Pd(CF_3CO_2)_2]$	γ-Al_2O_3-c	0.128	0.62		3.88	$Pd^0 >>> Pd^{II}$
				Cl/Pd	**N/Pd**		
G-WI-9	$[PdCl_2(PhCN)_2]$	γ-Al_2O_3-d	0.164	0.05	0.021	5.02	$Pd^{II} >>> Pd^0$
G-WI-10	$[PdCl_2(PhCN)_2]$	γ-Al_2O_3-c	0.174	0.034	0.019	5.35	$Pd^{II} >>> Pd^0$

was detected by XPS in addition to fluorescence observed by Raman spectroscopy meaning that decomposition took place on both aluminas. For $[PdCl_2(PhCN)_2]$, the same observations as for $[Pd(CF_3CO_2)_2(bipy)]$ could be made. The two samples prepared from this precursor on the dried or calcined alumina presented a large amount of Pd(II) at their surface as analyzed by XPS. The N/Pd and Cl/Pd ratios were relatively low confirming the covalent grafting by ligand exchange (Table 4).

3.1.5. Samples prepared in ethanol and acetone on dried alumina as references

$Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ were contacted in ethanol or acetone with dried alumina under inert atmosphere (Table S3 in Supplementary Information). This has been tested in order to have reference observations with the precursors and solvents chosen for anchoring (see next section). The Raman spectra of the solid samples showed Pd(0) in the case of ethanol meaning that no interactions between the precursors and the support took place. The

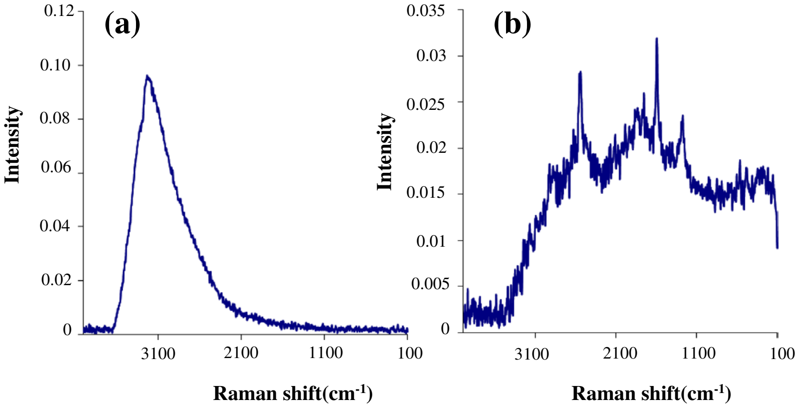


Figure 9. Raman spectra of (a) A-1$_{\_ref}$ and (b) A-8_Si^{1N}.

synthesis involving $Pd(OAc)_2$ in ethanol was repeated four times and the results were the same. The Raman spectrum of one of these samples showed the fluorescence signal due to the presence of Pd(0) (Figure 9), its presence being confirmed by XPS. When using acetone, the precursor peaks are observable on the Raman spectra indicating a direct grafting on the hydroxyl functions (see Figure S4 in Supplementary Material). The XPS analyses confirmed those observations: Pd(0) is present in the case of ethanol while Pd(II) was detected in the case of acetone. Analyses of filtrates by atomic absorption spectroscopy showed that in ethanol, the major part of the palladium was incorporated on the support compared to acetone where most Pd remained in solution.

In summary, grafting was successful for $[Pd(CF_3CO_2)_2(bipy)]$ on calcined alumina (G-WI-6), and for $[PdCl_2(PhCN)_2]$ on both treated aluminas (G-WI-9 and G-WI-10) with Pd(II) present at the surface after the syntheses. Direct grafting on surface OH groups was also successful on dried alumina using $Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ in acetone, but with a low yield.

3.2. Anchoring on functionalized supports

In order to facilitate precursor immobilization on the support, and to compare with grafting, the latter was functionalized with two different silanes to decorate the alumina surface with organic arms acting as anchoring points for the complexes, as depicted in Figures 1 and 2.

3.2.1. Support functionalization: characterization

The two silanes used for alumina functionalization (Figures 1 and 2) were chosen because of their ethoxy or methoxy groups which can be exchanged with the surface hydroxyl functions of the support as shown in Figures 1(a) and 2(a), respectively. In addition, their amine dangling functions can serve as ligands for Pd(II) as shown in Figures 1(c) and 2(c). The supports γ-Al_2O_3-1N and γ-Al_2O_3-2N obtained after reaction with the silanes have been analyzed by Raman spectroscopy, XPS, and ICP in order to check if the functionalization was successful. On both Raman spectra, a new peak appeared at 2900 cm^{-1} corresponding to C-H bonds indicating silane presence at the surface. Nitrogen and silicon were detected on the alumina surface by XPS. In addition, the N/Si surface ratio was 0.85 for γ-Al_2O_3-1N and 1.6 for γ-Al_2O_3-2N corresponding roughly to the nominal N/Si ratios in the starting silanes.

The γ-Al_2O_3-1N sample gave a C/N bulk molar ratio measured by ICP of about six, which is situated between the two extremes of three if the silane exchanged the three ethoxy functions and nine corresponding to no reaction, showing partial exchange of the ethoxy functions for surface groups, as desired. Besides, we observed the presence of almost 3 wt.% of Si showing that a good amount of silane was grafted on the support. From the ICP results and knowing the surface area ($S_{BET} = 60\ m^2/g$), we calculated 10 atoms of Si per nm^2 of functionalized alumina for the 1N support.

3.2.2. Anchoring of the precursors on the functionalized supports

$Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ have been used to study the anchoring of Pd complexes on the two functionalized alumina. Ethanol and acetone were used as solvents as described [15]. The samples obtained were analyzed by Raman spectroscopy and XPS to determine whether the anchoring took place and to quantify the amount of Pd present on the support surface.

3.2.2.1. Alumina functionalized with 3-aminopropyltriethoxysilane (γ-Al_2O_3-1N). Both $Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ precursors were contacted with the functionalized alumina γ-Al_2O_3-1N in acetone or in ethanol. On the Raman spectrum of A-8_Si^{1N} prepared with $Pd(OAc)_2$ in acetone, the peaks corresponding to the precursor are lost in the noise. The XPS results showed that Pd(II) is present in this sample confirming that the desired anchoring took place.

For $Pd(CF_3CO_2)_2$, fluorescence in Raman spectrum was observed when carrying out the anchoring in ethanol (A-13_Si^{1N} – Figure 10(a)) and 4.3 atomic % of Pd(0) was detected by XPS. For A-11_Si^{1N}, prepared in acetone, no signal was observed by Raman (Figure 10(b)) and only 0.61 atomic % of Pd was evidenced by XPS on the surface (Table 5). However, palladium in the latter catalyst exhibited the desired Pd(II) oxidation state and the F/Pd ratio was ~ 3, indicating the loss of one ligand and thus proving the anchoring of the precursor onto the silane arm.

In conclusion, no anchoring took place in ethanol probably because of the reducing character of this solvent. Acetone is assumed to wash away the non-anchored complex which remained mostly in the filtrate, but the Pd obtained in the solid corresponds to anchored complexes.

3.2.2.2. Alumina functionalized with N-[3-(trimethoxysilyl)propyl]ethylenediamine (γ-Al_2O_3-2N). As an attempt to improve anchoring, another functionalized alumina presenting a chelating ligand (noted 2N) has been used with $Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ as precursors both in acetone and ethanol. Again the samples prepared in ethanol presented fluorescence in Raman spectroscopy due to Pd(0). For A-10_Si^{2N} prepared in acetone with $Pd(OAc)_2$, the peaks corresponding to the silane were present in the Raman spectrum. An additional peak was observed as well corresponding to the intact precursor (Figure 11(b)). The XPS results of this sample showed the presence of Pd(II) and as previously a smaller amount of Pd at the surface than in the sample prepared in ethanol. The other material prepared in acetone, A-12_Si^{2N}, did not show any peak in the Raman spectrum but showed a weak amount of Pd(II) at the surface, with a F/Pd ratio situated between 2 and 3 proving the anchoring in this case.

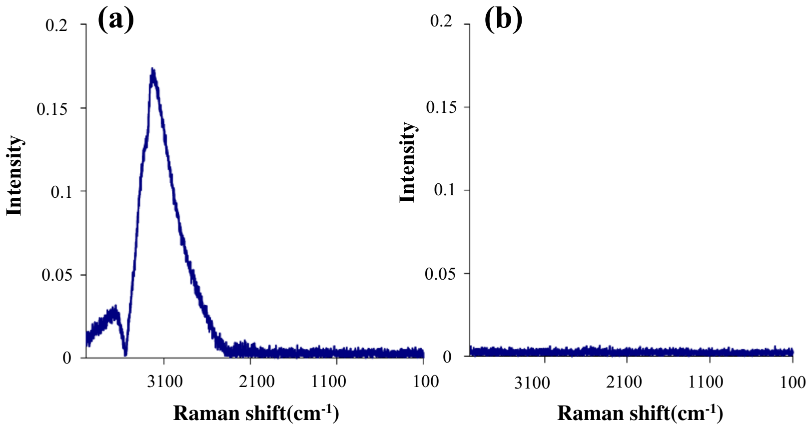


Figure 10. Raman spectra of (a) A-13_Si^{1N} and (b) A-11_Si^{1N}.

Table 5. XPS results for the anchoring of [Pd(CF_3CO_2)$_2$] on γ-Al_2O_3-1N support.

Code	% at. Pd	Pd^0/Pd^{II}	Pd/Al	% at. Si	F/Pd
A-11_Si^{1N}	0.61	Pd^{II}>>>Pd^0	0.02	2.18	2.6
A-13_Si^{1N}	4.33	Pd^0>>>Pd^{II}	0.157	1.87	0.25

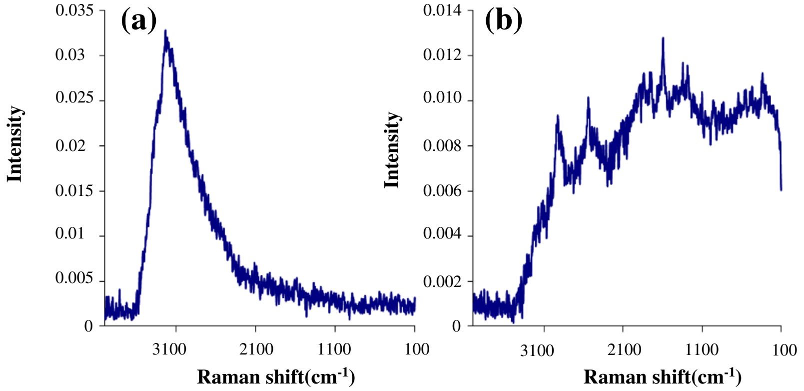


Figure 11. Raman spectra of (a) A-9_Si^{2N} solid and (b) A-10_Si^{2N}.

3.3. Activation of the samples

In order to evaluate if Pd metal could be obtained at the catalyst surface for future use in specific reactions in which Pd(0) is the active phase, the samples were reduced under hydrogen. The working hypothesis was that the grafted/anchored samples would give higher dispersion of the active phase thanks to hindering of Pd migration. The catalysts prepared by grafting were characterized by XPS after activation and as expected Pd was mainly present as Pd(0) except for G-WI-9a (Table 6) where it remained in Pd(II) form. For the sample G-WI-10a, Pd(II) was also the main component of the Pd3d photopeak. This is correlated with

Table 6. XPS results for the reduced catalysts prepared by grafting.

			XPS : fresh catalysts		XPS : reduced catalysts		
Code	Precursor	Solvent	% Pd	Pd^0/Pd^{II}	% Pd	Pd^0/Pd^{II}	Pd/Al
G-WI-3a	$[Pd(acac)_2]$	Toluene	1.80	$Pd^0 >>> Pd^{II}$	0.374	$Pd^0 >>> Pd^{II}$	0.010
G-WI-6a	$[Pd(CF_3CO_2)_2(bipy)]$	Acetonitrile	1.60	Pd^{II}	0.072	Pd^0	0.002
G-WI-7a	$[Pd(CF_3CO_2)_2]$	Acetonitrile	4.74	$Pd^0 >>> Pd^{II}$	0.377	Pd^0	0.011
G-WI-8a	$[Pd(CF_3CO_2)_2]$	Acetonitrile	3.88	$Pd^0 >>> Pd^{II}$	0.269	Pd^0	0.008
G-WI-9a	$[PdCl_2(PhCN)_2]$	Acetonitrile	5.02	$Pd^{II} >>> Pd^0$	0.196	Pd^{II}	0.007
G-WI-10a	$[PdCl_2(PhCN)_2]$	Acetonitrile	5.35	$Pd^{II} >>> Pd^0$	0.366	$Pd^{II} >> Pd^0$	0.013

Table 7. XPS results after activation for the reference samples and for the catalysts prepared by anchoring.

					XPS results			
Code	Support	Precursor	Solvent	Pd loading (%)	% Pd	Pd^0/Pd^{II}	Pd/Al	F/Pd
A-1a$_{\_ref}$ [a]	γ-Al_2O_3-d	$[Pd(OAc)_2]$	Ethanol	3.47	1.050	Pd^0	0.036	n.d.
A-2a$_{\_ref}$	γ-Al_2O_3-d	$[Pd(OAc)_2]$	Acetone	1.10	0.369	Pd^0	0.011	n.d.
A-3a$_{\_ref}$	γ-Al_2O_3-d	$[Pd(CF_3CO_2)_2]$	Ethanol	4.94	0.696	Pd^0	0.025	3.63
A-4a$_{\_ref}$	γ-Al_2O_3-d	$[Pd(CF_3CO_2)_2]$	Acetone	*traces*	0.091	$Pd^0 \approx Pd^{II}$	0.003	24.9
A-8a_Si^{1N}	γ-$Al_2O_{3-1}N$	$[Pd(OAc)_2]$	Acetone	1.07	0.507	$Pd^0 >>> Pd^{II}$	0.018	n.d.
A-9a_Si^{2N}	γ-$Al_2O_{3-2}N$	$[Pd(OAc)_2]$	Ethanol	3.95	1.221	$Pd^0 >>> Pd^{II}$	0.040	n.d.
A-10a_Si^{2N}	γ-$Al_2O_{3-2}N$	$[Pd(OAc)_2]$	Acetone	1.11	0.552	$Pd^0 \approx Pd^{II}$	0.020	n.d.
A-11a_Si^{1N}	γ-$Al_2O_{3-1}N$	$[Pd(CF_3CO_2)_2]$	Acetone	0.34	0.541	$Pd^0 \approx Pd^{II}$	0.018	2.42
A-12a_Si^{2N}	γ-$Al_2O_{3-2}N$	$[Pd(CF_3CO_2)_2]$	Acetone	0.71	0.637	$Pd^0 \approx Pd^{II}$	0.023	1.34
A-13a_Si^{1N}	γ-$Al_2O_{3-1}N$	$[Pd(CF_3CO_2)_2]$	Ethanol	4.87	3.666	Pd^0	0.144	0.271
A-14a_Si^{2N}	γ-$Al_2O_{3-2}N$	$[Pd(CF_3CO_2)_2]$	Ethanol	4.93	3.641	Pd^0	0.135	0.129

[a] Average values over four different samples.

successful grafting of the complex in these particular cases, which as a consequence is stabilized in Pd(II) form, preventing its reduction.

As for the catalysts prepared by grafting, the samples synthesized by anchoring on the functionalized supports were activated thermally and characterized by XPS (Table 7). All the reduced catalysts had Pd(0) at the surface. However, in most cases, Pd(II) was also present in significant proportion. The amount of Pd (at.%) measured on the catalyst surface was always higher when prepared in ethanol. This is in line with the higher Pd content in these catalysts before reduction.

3.4. Discussion

We have shown that grafting or anchoring of Pd complexes could take place on alumina, but only by adjusting carefully the reaction conditions employed. Concerning the wet impregnation method in which the precursor and the support were brought in contact in a solvent suitable to solubilize the precursor, the grafting did not occur at room temperature, except in acetone in very low yield. However, when the wet impregnation method was carried out under inert atmosphere and refluxing conditions, the grafting succeeded in some additional cases. Indeed, ligand exchange between the precursor and OH groups of the support surface was observed by XPS and Raman spectroscopy when the reaction was carried out in acetonitrile with $[Pd(CF_3CO_2)_2(bipy)]$ and $[PdCl_2(PhCN)_2]$. However, when these two samples (G-WI-9 and G-WI-10) were heated under reducing conditions, Pd(0) was not obtained at the surface. This highlights the fact that a grafting reaction effectively occurred for these two samples but that the Pd(II) species are very stable at the support surface. These two samples would be more advantageously used in homogeneous supported catalysis, in a reaction requiring Pd(II) as active phase.

For the anchoring part of the study, we were able to functionalize gamma alumina support by grafting two different silanes on its surface. The two Pd complexes $Pd(OAc)_2$ and $Pd(CF_3CO_2)_2$ were successfully anchored when the reactions were carried out in acetone, on both functionalized supports. These were reduced and presented mainly Pd(0) at the support surface in the final materials. Hence, the anchoring procedure does not lead to retardation in the reduction process in contrast to direct grafting onto hydroxyl groups.

By contrast, the samples prepared in ethanol presented a large amount of reduced palladium at their surfaces in all cases. However, this was not obtained after activation but right from the precursor stage where the reducing ability of ethanol prevented a neat surface reaction and preservation of Pd(II) state but led to formation of Pd(0) phase rather than ligand exchange for the silane dangling arm.

The methodology developed in this work to prove the success of the grafting and anchoring processes on alumina was reliable. We were able to find suitable conditions to graft and anchor Pd complexes on alumina surface and also able to show when grafting or anchoring did not occur by providing direct experimental evidence of alternative mechanisms taking place, such as reduction by the solvent in the case of ethanol, or complex decomposition in the case of wet impregnation carried out in air. In many instances, even if carrying out an experimental procedure aiming at grafting or anchoring, the desired surface reaction did not occur. This demonstrates that these two terms should not be used too freely if no experimental proof of ligand exchange is gathered in the supported samples. A careful selection of metal compound nature, solvent, and support surface state is a key to control such reactions occurring at the solid/solution interface.

4. Conclusion

The aim of this work was to provide deeper insight into the formation processes of palladium catalysts supported on γ-Al_2O_3, from a coordination chemistry point of view. Two methodologies were investigated: on the one hand, the direct grafting of Pd complexes onto hydroxyl functions present at the surface of alumina and on the other hand, precursors anchoring via amine-bearing silanes previously grafted on the support. The results showed that covalent grafting took place for samples synthesized in acetonitrile from $[Pd(CF_3CO_2)_2(bipy)]$ and $[PdCl_2(PhCN)_2]$ on a gamma alumina previously heated in air or under vacuum. Grafting was also successful when $Pd(OAc)_2$ or $Pd(CF_3CO_2)_2$ were contacted in acetone with dried alumina. In all cases, less than 1 wt.% of Pd could be incorporated on the support as molecular Pd(II) fragments. Concerning the second part of this work, the anchoring was proven for catalysts prepared in acetone with also 1 wt.% of Pd(II) obtained at the surface. In other cases, the Pd complexes decomposed during the impregnation step and Pd(0) was found at the surface without the use of external reducing agent, except the solvent itself in some cases.

This study highlights the importance of choosing the appropriate experimental conditions, such as type of metal precursor, state of support surface, choice of solvent, atmosphere of impregnation, temperature, *etc.*, to obtain a surface ligand exchange reaction. By selecting the synthesis conditions, we were able to prepare catalysts by grafting or anchoring. In addition, we have obtained direct experimental evidence of grafting and anchoring successes in some cases, and demonstrated that it formally did not occur in other cases.

The successfully grafted samples were difficult to reduce and displayed Pd(II) stabilized at the support surface even after heating under hydrogen. By opposition, the anchored samples, after thermal activation, presented mostly Pd(0) at their surface. This shows that reduction hindering is due to the formation of direct Pd-O-Al bonds.

These Pd/alumina catalysts are ideal candidates for heterogeneous catalytic processes in which the stability of the active phase is crucial for the process viability. Indeed, when grafting or anchoring is employed to prepare catalysts, the stability of the active phase in terms of sintering is higher than when simple impregnation method with no optimization of the metal/surface interactions is employed.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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