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# Synthesis and study of the catalytic applications in C-C coupling reactions of hybrid nanosystems based on alumina and palladium nanoparticles

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### Abstract

Nanostructured alumina has been treated under mild conditions with different quantities of [PdCl<sub>2</sub>(cod)] (cod = 1,5-cyclooctadiene) to promote the formation of supported palladium nanoparticles which have been characterized by XRD, XRF, BET and TEM. The results show that the new hybrid materials, **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**, consist of impregnated palladium nanoparticles onto aggregates of nanoparticles of alumina. The catalytic activity of the hybrid Pd-alumina materials has been tested in Suzuki-Miyaura C–C coupling reactions observing good conversion rates in the reactions of 3-bromoanisole with 4-carboxyphenylboronic acid or 4-vinylphenylboronic acid. The catalytic studies have been extended with experiments investigating the Pd loading influence. Catalyst recyclability tests show a slight decrease in activity after the first cycle in the reaction of 3-bromoanisole with 4-vinylphenylboronic acid. However, subsequent activity remains almost constant after five more consecutive catalytic cycles.

### Keywords

Pd nanoparticles; alumina; Suzuki-Miyaura C-C coupling reactions; catalysis; recyclability

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### 1. Introduction

The current use of metal nanoparticles has been extended to a wide variety of applications such as non-linear optics, medical dressings and catalysis among others [1,2,3,4]. In many cases especially when the final application is catalysis, metal nanoparticles are being supported on different materials ranging from organic polymers [5] to various transition metal oxides [6], mesoporous silica materials [1], alumina and microporous zeolites [7].

Specifically alumina-based materials have found various applications [8] in adsorption, hostguest encapsulation and most notably in catalysis [9]. This is due to their optimal textural properties, acid-base characteristics, thermal and chemical stability and low price. All these properties make alumina one of the most promising candidates as a support for industrial catalysts [10,11]. One however should take into account that the final physical properties and catalytic activity of alumina-based catalysts are highly dependent on the starting support and the synthetic methods for the deposition of the active species such as metal complexes or metal nanoparticles [10,12].

In the case of hybrid catalytic systems based on supported metal nanoparticles, the incorporation and position of the active centers located on the external surface area of the metal nanoparticles of the hybrid material is very important. Thus, an effective loading of metal nanoparticles is required for the preparation of highly active systems [13,14]. In addition, a rigorous control of the size and morphology of the supported nanoparticles is needed, bearing in mind that these parameters must be kept stable during and after the catalytic cycle, to prevent particle agglomeration [12].

Presently, the most effective supported hybrid catalysts are synthesized using two different methods: 1) during the preparation of the support by co-precipitation, co-condensation or in situ reduction methods or 2) by post-synthetic treatment of the surface with metal precursors. In the case of Pd nanoparticles the most common precursor for the post synthetic method is palladium acetate and its subsequent reaction with reducing agents such as ethanol, NaBH4, H2 and hydrazine [1,2,12]. Alternative methods include ion exchange with metal precursors [15], adsorption of molecular cluster precursors [16], immobilization of metal complexes [17] or photocatalytic reduction [18]. The synthetic method used for the support of the nanoparticles is very important, as it may change the nature of the interaction between active species (metal nanoparticles) and the supporting material. This is crucial in proposing and understanding catalytic mechanisms for the hybrid systems. Hence, certain methods may lead to incorporation of the nanoparticles within the structure of the materials [19] while others may lead to systems with simple impregnation of the metal nanoparticles in the support [1]. Accordingly, intense studies have been carried out by several groups and many different methods have been reported for the effective and green preparation of well-dispersed supported metal nanoparticles[20] which have subsequently been used in C-C coupling reactions [2]. In this context, a wide variety of Pd-supported systems based on mesoporous silica have been

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reported [19,21,22,23,24,25,26,27,28] and have demonstrated moderate to excellent activities in C-C coupling reactions [29]. However, the activity of these systems normally decreases after the first catalytic cycle due to their structure collapsing and agglomeration of the active species (metal nanoparticles) [24].

Although alumina supported Pd nanoparticles have been studied in numerous catalytic reactions [30,31,32,33], the most exploited catalytic application is that of C-C coupling [34,35,36,37,38,39]. As a continuation of our previous work [24], herein we report the preparation of similar systems starting from an organometallic palladium precursor such as [PdCl<sub>2</sub>(cod)] which is reduced *in situ* in a single step to give dispersed supported Pd-nanoparticles. The synthesized materials were tested in specific C-C coupling Suzuki-Miyaura reactions, namely 3-bromoanisole with 4-carboxyphenylboronic acid or 4-vinylphenylboronic acid. The catalytic tests showed good activity and, notably, a significantly high degree of recyclability in the reaction between 3-bromoanisole and 4-vinylphenylboronic acid. The catalytic versatility of these hybrid systems has proven to be very useful for the preparation of fine chemicals namely the final products of the coupling reactions between 3-bromoanisole and 4-carboxyphenylboronic acid or 4-vinylphenylboronic acid, which are now being used in our group as linker ligands for the preparation of different MOFs.

#### 2. Experimental

#### 2.1. General conditions

All manipulations were performed under dry nitrogen gas using standard Schlenk techniques and dry box. Solvents were distilled from the appropriate drying agents and degassed before use. Aluminum oxide – nanopowder (<50 nm particle size (TEM)) (Sigma-Aldrich) was used as purchased, with a simple dehydration process (see section 2.3.2). Water (resistance 18.2 M $\Omega$ cm) used in the preparation of materials was obtained from a Millipore Milli-Q-System (Billerica, MA, USA).

### 2.2 General remarks on the characterization of the materials

X-ray diffraction (XRD) patterns of the hybrid materials were obtained on a Philips Diffractometer model PW3040/00 X'Pert MPD/MRD at 45 KV and 40 mA, using a wavelength Cu K $\alpha$  ( $\lambda$  = 1.5418 Å). Pd wt % determination by X-ray fluorescence were carried out with a X-ray fluorescence spectrophotometer Philips MagiX with an X-ray source of 1 kW and a Rh anode using a helium atmosphere. The quantification method is capable of analyzing from 0.0001% to 100% Pd. N<sub>2</sub> gas adsorption-desorption isotherms were performed using a Micromeritics ASAP 2020 analyzer. Conventional transmission electron microscopy (TEM) was carried out on a TECNAI 20 Philips, operating at 200 kV.

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### 2.3. Preparation of the hybrid materials nano-Al<sub>2</sub>O<sub>3</sub>-Pd-X

### 2.3.1. Synthesis of Pd nanoparticles precursor: [PdCl<sub>2</sub>(cod)]

 $PdCl_2$  (3.05 g, 17.2 mmol) was dissolved in 8 mL of concentrated HCI. The cooled solution was diluted with 250 mL of absolute ethanol and passed through a filter paper; the residue and filter paper were then washed with 40 mL of ethanol. Afterwards, 1,5-cyclooctadiene (5.0 mL, 40.7 mmol) was added to the resulting solution under stirring. The solution turned from brown to deep yellow and the solid product precipitated immediately. The reaction was stirred for an additional 15 min and then filtered and the yellow solid washed with diethylether (3 × 20 mL). The final product was dried under vacuum overnight giving 4.80 g (16.8 mmol) of  $[PdCl_2(cod)]$  (yield: 98%).

### 2.3.2. Alumina activation

Before the functionalization reactions, the alumina needs to be activated. The activation consists in the dehydration and elimination of the physisorbed solvents on the hydroxyl functional groups present on the surface by the treatment of the corresponding material under vacuum conditions for 24 h at 150 C.

### 2.3.3. Synthesis of nano-Al<sub>2</sub>O<sub>3</sub>-Pd-X materials

Several hybrid materials have been synthesized by the functionalization of alumina through the reduction of the palladium precursor [PdCl<sub>2</sub>(cod)]. Table 1 shows the quantity of palladium complex and alumina employed in each reaction.

The general procedure carried out for the preparation of the hybrid materials was similar to that described previously by our group [24]: in a dry box, the corresponding amount of the alumina and [PdCl<sub>2</sub>(cod)] were added to a Schlenk tube and dried under vacuum for 1 h at room temperature. Subsequently, 30 mL of tetrahydrofurane (THF) was added under an inert atmosphere. The reaction mixture was then heated to 80 °C and stirred for 48 h. The optimum reaction conditions were determined by carrying out the synthesis at different temperatures, reaction times and solvents and this showed that the greatest efficacy was obtained using THF as solvent, at 80 °C and a reaction time of 48 h. Subsequently, the hybrid material was filtered and washed several times with THF, water and diethylether (2 × 50 mL each). Finally, the material was dried under vacuum for 12 hours to remove all trace of solvent. This procedure was repeated for each of the initial amounts of palladium used in the preparation of the different hybrid materials.

### 2.4. Catalytic studies

### 2.4.1. Preliminary tests

Catalytic tests were focused on two reactions:

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- 1) Reaction between 3-bromoanisole and 4-carboxyphenylboronic acid (Scheme 1)
- 2) Reaction between 3-bromoanisole and 4-vinylphenylboronic acid (Scheme 2)

The reactions were performed under identical conditions in order to facilitate a subsequent analysis of the results. The limiting reagent was the halide derivative, the molar ratio between the boronic acid and the halide was 1:1.5, the molar ratio between the base (K<sub>2</sub>CO<sub>3</sub>) and the halide was 2:1 and the amount of catalyst was 5, 10 or 15 mg depending on the reaction and the parameters being studied. Degassed solvents and a nitrogen atmosphere were used in the reaction to achieve higher final conversions [28].

In a typical catalytic reaction a three-neck flask was filled with 4-carboxyphenylboronic acid (33.16 mg, 0.200 mmol) or 4-vinylphenylboronic acid (29.59 mg, 0.200 mmol),  $K_2CO_3$  (36.95 mg, 0.267 mmol) and Pd catalyst (10 mg) and three vacuum/N<sub>2</sub> cycles (10 min/1 min) under stirring were applied to remove oxygen from the reaction atmosphere and adsorbed water from the ambient. In parallel, the solvent (DMF:H<sub>2</sub>O 95:5, 50 mL) and the aryl halide (25 mg, 0.133 mmol) were mixed under nitrogen in a Schlenk tube, bubbling N<sub>2</sub> inside the solution for 15 min to eliminate dissolved oxygen. Subsequently, this mixture was transferred under N<sub>2</sub> to the three-neck flask containing the solid mixture. The suspension was then heated to the corresponding temperature (using a condenser in the case of refluxing conditions) and stirred for 48 h. The reaction was monitored by extracting 250 µL of sample at different reaction times (0, 1, 2, 4, 24 and 48 h). After this time, the solution was cooled to room temperature, filtered and the solvent of the filtrate removed under vacuum. The catalytic activity of the synthesized materials in the Suzuki-Miyaura coupling reactions has also been compared to the activity of a homogeneous Pd catalyst, [Pd(PPh<sub>3</sub>)<sub>4</sub>] using 1% Pd.

### 2.4.1.1. Purification of the catalytic products

The purification of the product was achieved using a chromatographic column, charged with silica gel and the suitable eluent to separate the reaction product. The latter was chosen on the basis of tests carried out on thin layer chromatography (TLC).

For reaction 1 (3-bromoanisole + 4-carboxyphenylboronic acid), dichloromethane:toluene (9:1) was used as the eluent solution. Solvent was removed from the solution containing the product with a rotavapor and the light yellow solid obtained was dried overnight at 60  $^{\circ}$ C under vacuum and analyzed by <sup>1</sup>H-NMR showing the same signals that were previously reported for the product of this reaction [24].

For reaction 2 (3-bromoanisole + 4-vinylphenylboronic acid) hexane:dichloromethane (7:3) was used as the eluent solution and the R<sub>f</sub> of the compound is 0.32. Solvent was removed from the solution containing the product (Figure 1) with a rotavapor and the yellow solid obtained was dried at 60 °C under vacuum overnight. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.90 (s, 3H, O*Me*), 5.31 (dd, <sup>2</sup>J<sub>BC</sub> = 1 Hz and <sup>3</sup>J<sub>BA</sub> = 11 Hz, 1H, CH=CH<sub>2</sub>  $\rightarrow$  H<sub>b</sub>), 5.82 (dd, <sup>2</sup>J<sub>CB</sub> = 1 Hz and

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 ${}^{3}J_{CA}$  = 17.5 Hz, 1H, CH=CH<sub>2</sub> → H<sub>c</sub>), 6.79 (dd,  ${}^{3}J_{AB}$  = 11 Hz and  ${}^{3}J_{AC}$  = 17.5 Hz, 1H, CH=CH<sub>2</sub> → H<sub>a</sub>), 6.92 (dd appears as a pseudo t, 1H, *H* in C6), 7.16 (pseudo t, 1H, *H* in C2), 7.22 (d, 1H, *H* in C4), 7.38 (m, 1H, *H* in C5), 7.51 (d,  ${}^{3}J$  = 8.0 Hz, 2H, *H* in C9) and 7.59 (d,  ${}^{3}J$  = 8.0 Hz, 2H, H in C8) ppm.  ${}^{13}C{}^{1}H$  NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 55.3 (OMe), 112.70 and 112.73 (C2 and C4), 114.0 (CH=*C*H<sub>2</sub>), 119.5 (C6), 126.6 (C9), 127.3 (C8), 129.8 (C5), 136.4 and 136.8 (C1 and C7), 140.5 (C10), 142.3 (*C*H=CH<sub>2</sub>), 160.0 (C3) ppm.

#### 2.4.1.2. Quantification of the conversion rate

The technique employed to quantitatively analyze the conversion of 3-bromoanisole and to identify the reaction product was gas chromatography (GC) with FID detector (Varian CP-3370) using a 15 m CP-SIL-8 column provided by Scharlau. The kinetics or the conversion of the different reactions was determined by following the variation of the concentration of 3bromoanisole in solution. To follow the changes of the halide concentration, an internal standard compound (1-octanol) was used. Comparing the areas relating to the signals of the halo compound and the internal standard, the concentration of the halide can be determined with accuracy. The chosen internal standard was 1-octanol (100 ppm), an inert compound with respect to reagents and products and that has a different retention time than the other compounds. The solution samples to be analyzed were diluted in the ratio 1:50 in order to adjust the concentration of reactants and products to the range of linearity of the calibration curve. The calibration curve was prepared using a concentration of halide in the range 0-500 ppm for both reactions. The temperature conditions were: injector temperature: 240 °C, detector temperature: 250 °C, oven temperature program 110 °C (10 min); from 110 °C to 240 °C (with a ramp of 10 ℃/min) and 240 ℃ (15 min). Operating under these conditions the retention times of the chemical species in solution were, DMF: 3.0 min, 1-octanol: 5.8 min, 3-bromoanisole: 11.5 min, 4-carboxyphenylboronic acid: 18.5 min, 4-vinylphenylboronic acid: 16.81 min, product of the first reaction: 20.17 min, product of the second reaction 19.9 min. The tests were carried out in triplicate, (the reported results are the average of those obtained). For an example of a chromatogram of the reaction between 3-bromoanisole and 4-vinylphenylboronic acid see Figure S1 of the Supplementary Material.

### 2.4.2. Catalytic study of the influence of Pd quantity

Additional catalytic tests have been carried out to study the conversion of the 3-bromoanisole in both reactions, firstly with 4-carboxyphenylboronic acid and subsequently with 4-vinylcarboxyphenylboronic acid using different amounts of catalyst. The conversion studies were carried out using 15 mg and 5 mg of each of the following catalysts: **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-20** and **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-50**. Conversion experiments were performed in a single-neck Schlenk tube. Solution samples were collected and analyzed at the beginning and at the end of the reaction time.

In a typical catalytic reaction a single-neck flask was filled with 4-carboxyphenylboronic acid (9.95 mg, 0.060 mmol) or 4-vinylphenylboronic acid (8.90 mg, 0.060 mmol),  $K_2CO_3$  (11.05 mg,

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0.080 mmol) and Pd catalyst (5 or 15 mg in each case) and three vacuum/N<sub>2</sub> cycles (10 min/1 min) under stirring were applied. In parallel, the solvent (DMF:H<sub>2</sub>O 95:5, 15 mL) and the aryl halide (7.50 mg, 0.040 mmol) were mixed under nitrogen in a Schlenk tube, bubbling N<sub>2</sub> inside the solution for 15 min. Subsequently, this mixture was transferred under N<sub>2</sub> to the three-neck flask with the solid mixture. The suspension was then heated to the corresponding temperature (using a condenser in the case of refluxing conditions) and stirred for 48 h, then, the reaction was monitored by extracting 250  $\mu$ L of sample. Product isolation was carried out following a similar procedure to that described in the section 2.4.1.

### 2.4.3. Study of the catalyst recyclability

Additional catalytic tests were carried out to determine the loss of activity of the catalysts after several catalytic cycles. Recyclability tests were carried out using similar experimental procedures but tested in up to five catalytic cycles in a row using **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**. The reactions were therefore performed on a larger scale, under the same experimental conditions. The tests were conducted using a higher amount of catalyst (1.0 g) in order to be able to carry out five catalytic cycles. After each cycle, the catalyst was filtered and washed with water (2 × 100 mL) and diethylether (2 × 30 mL). The final amounts of reactants used in the different recyclability tests are shown in Table S1 of the Supplementary material.

### 3. RESULTS AND DISCUSSION

### 3.1. Synthesis and characterization of supported palladium nanoparticles

### 3.1.1. Synthesis of supported palladium nanoparticles

Commercial nanorods of alumina were treated with increasing amounts of [PdCl<sub>2</sub>(cod)] in THF during 48 hours to give supported palladium nanoparticles which were formed *via* the reduction of [PdCl<sub>2</sub>(cod)] in a similar process to that described previously by our group for silica- and titania-based materials [24,40,41]. Thus, the reduction of the organometallic palladium complex is achieved by THF which, together with the hydroxyl groups at the surface of the materials, acts as the reducing agent. According to the TEM images, it seems clear that once the palladium nanoparticles are formed, they remain impregnated on the external surface of the alumina support, presumably via interaction with the -OH groups of alumina.

### 3.1.2. Characterization by X-ray Fluorescence

A Pd-loading study of the nanostructured alumina has been carried out using different amounts of [PdCl<sub>2</sub>(cod)]. The Pd content was determined by X-ray fluorescence analysis. Theoretical 1, 2, 5, 10, 20 and 50% wt. Pd was used for each reaction. A study of the hypothetical saturation level and efficacy of Pd incorporation was calculated for all the synthesized materials.

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Thus, using these Pd amounts, the maximum percentage of incorporated palladium was in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** with a Pd content of 21.4% wt. which was obtained when starting from theoretical 50 % wt. Pd. It is important to note that the data from all the experiments showed a potential trend in the studied loading range (see Figure S2 of Supplementary Material for the graphs and trend equation adjust). However, according to the graphical representation of the equation, a maximum of saturation is expected when using higher amounts of Pd. These materials showed higher loading capacities than other silica-based materials reported previously [24].

#### 3.1.3. Characterization by N<sub>2</sub> adsorption-desorption

The unmodified alumina, **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** were characterized by N<sub>2</sub> adsorption-desorption isotherms (BET method), which allowed the determination of the specific surface area and pore size distribution of the studied materials. The measurements showed type II isotherms according to the IUPAC classification [42] for the alumina (Figure S3 of the supplementary material), as well as their corresponding Pd-impregnated materials (**nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** (Figure 2a) and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** (Figure 2b)). These isotherms are indicative of non-porous or macroporous materials. The only difference in the isotherms observed after Pd-functionalization was a decrease in the surface area (Table 2), which indicates that Pd nanoparticles are impregnated onto the materials. Pore size distribution is not regular for any of the materials, and the incorporation of Pd nanoparticles does not have a significant effect on this parameter.

### 3.1.4. Characterization by X-ray Diffraction

The XRD pattern of the amorphous alumina did not present any peaks. However, for all the Pdfunctionalized hybrid materials, high angle X-ray diffractograms (Figure S4 of supplementary material) showed peaks at 20 of 39.3, 45.4, 67.4, 80.3, 84.7<sup>o</sup> associated to the (111), (200), (220), (311) and (222) planes of palladium nanoparticles, respectively [43].

### 3.1.5. Characterization by TEM

The unmodified alumina as well as the materials **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** have been characterized by Transmission Electronic Microscopy (TEM). The TEM image of alumina shows that this material is composed of submicronic agglomerates of nanorods of up to 100 nm long (Figure S5 of supporting information). However, after the functionalization with the Pd nanoparticles one can easily observe the palladium nanoparticles as black dots impregnated on the external surface of the alumina support as is the case of materials **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** (Figure 3a) and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** (Figure 3b). Palladium nanoparticles are "quasi-spherical" and have diameters of 38±12 and 43±18 nm for **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**, respectively. Pd nanoparticle sizes have been calculated by using the software ImageJ (for the particle size distribution see Figures S6 and S7 of the Supplementary Material). In addition, it seems clear that the larger palladium particles are formed by clusters of very small Pd

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nanoparticles. In spite of what has been observed previously for similar hybrid systems based on mesoporous silica [24], for the alumina-based materials, reaction time has no influence on the morphology and location of palladium nanoparticles. This is because the support material is not porous and the formation of the Pd-nanoparticle is not based on its previous accumulation inside a pore, but on its formation on the external surface area of the alumina (see Figure S8 for a TEM image of the material obtained after 6 hours of reaction). In addition, in these systems, palladium nanoparticles do not show a high tendency to aggregate, but remain partially dispersed on the surface of the alumina with a relatively homogeneous dispersion of the metal.

### 3.2. Catalytic tests

#### 3.2.1. Preliminary catalytic tests in Suzuki-Miyaura C-C coupling reactions

The material **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** was tested in two coupling reactions of two different boronic acids (4-carboxyphenylboronic acid and 4-vinylphenylboronic acid) with 3-bromoanisole. In addition, a homogeneous commercial catalyst  $[Pd(PPh_3)_4]$  was also used for comparison of each reaction. All the catalytic tests were carried out under experimental conditions described previously by our group [24], using a DMF/H<sub>2</sub>O (95:5) mixture as solvent, K<sub>2</sub>CO<sub>3</sub> as base and measuring the final conversion at 0, 1, 2, 4, 24 and 48 hours after starting the reaction. The temperature was set at 70  $^{\circ}$ C as we previously observed this be optimal for the catalytic tests [24].

Table 3 shows the results obtained in the preliminary tests, for the reaction between 3bromoanisole and 4-carboxyphenylboronic acid (Scheme 1) and between 3-bromoanisole and 4-vinylphenylboronic acid (Scheme 2) at different time intervals. Both reactions showed similar behavior reaching almost the maximum level of halide conversion after 4 hours followed by a much slower decrease until the end of the reaction time. However, the reaction using 4carboxyphenylboronic acid (Scheme 1) seems to be more effective than that of 4vinylphenylboronic acid (Scheme 2). This is presumably due to the difference in the electronic properties of the –COOH (electron-withdrawing inductive effect –*I*) and vinyl groups (electronreleasing effect +*I*) which make 4-carboxyphenylboronic acid more reactive towards  $K_2CO_3$  in the formation of the active species  $[ArB(OH)_3]^-$  which subsequently reacts with the Pdnanoparticles. In addition to the electronic properties one cannot ignore the acidic nature of the carboxylic acid group which may also increase the reactivity towards bases such as  $K_2CO_3$ leading to a more effective formation of species of the type  $[ArB(OH)_3]^-$ .

# 3.2.2. Study of the effect of Pd and catalyst quantity in Suzuki-Miyaura C-C coupling reactions

We have studied the influence of the Pd content on the catalytic activity using the materials nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20 and nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50 (Table 5). The results show that nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50

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with a higher amount of Pd gives higher conversion rates than **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-20**. However, the TOF are lower in the case of **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-50**, indicating a higher effectivity of **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-20**. We also performed some additional experiments using **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-1**, **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-2**, **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-5** and **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-10**, but using the same reaction conditions the results showed much lower conversions which were not worthy of subsequent investigation. Therefore our study is focused on materials **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-20** and **nano-Al**<sub>2</sub>**O**<sub>3</sub>-**Pd-50**.

In addition, some reactions using different quantities of catalysts (15 and 5 mg) were carried out observing in both cases (**nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**, Table 5), a higher catalytic efficiency (TOF) using 5 mg of catalyst than when using 15 mg of material. Furthermore, as expected, the halide conversion is lower when using 5 mg than when using 15 mg of catalyst. It is important to note that, in both cases (15 and 5 mg), the TOF are higher for **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20**, compared with **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**, indicating a higher effectivity of the former. In general, the TOF of the nanostructured hybrid catalysts **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** are comparable to those of the homogeneous system based on [PdCl<sub>2</sub>(PPh<sub>3</sub>)] over the studied reaction time.

### 3.2.3. Preliminary study of the recyclability of the catalysts

Catalyst recycling was investigated for **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**. Since the recovery of the catalyst in small quantities is very difficult, we designed experiments using greater amounts of catalyst but maintaining the molar ratio of all reactants and solvents. For both reactions a loss of activity of the catalysts was observed after the first recycle test (Figure 4). However, this loss of activity is much higher in the case of 4-carboxyphenylboronic acid (ca. 55%) compared to 4-vinylphenylboronic acid (ca. 10%). This is maybe due to two different effects. Firstly the possible agglomeration of the nanoparticles after the first cycle. This effect has previously been observed in similar hybrid systems based on silica [24]. However, the effect of the agglomeration would be expected to cause a similar degree of deactivation for both reactions. As the loss of activity when using 4-vinylphenylboronic acid is small, it can be assumed that agglomeration is not very significant. In fact, when one analyzes a TEM image of the recovered catalysts (**nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** and **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-vinyl-rec**) taken after the consecutive catalytic cycles and no significant differences were observed compared with the starting material **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** (See Figure S9 and S10 of supplementary material).

Therefore, the very high differences in the deactivation may be due to an additional effect related to the carboxyl functional group. A plausible explanation is that the formation of stable intermediate species of the type "Ar-Pd-OOC-Ar" (Pd(II) species) which are formed during the catalytic process and which may partially deactivate the Pd nanoparticles leading to lower conversions in the second and subsequent catalytic cycles as the active species should be based on Pd(0). It is important to note that the formation of these species is not possible in the case of 4-vinylphenylboronic acid as this compound does not have carboxylic groups.

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After the second catalytic cycle the halide conversions are similar, indicating the stabilization of the catalytic activity after the second catalytic cycle and pointing to a good degree of recyclability of the systems, especially when the reactions with 4-vinylphenylboronic acid. In addition, to confirm that the partial deactivation of the catalysts in the reaction with 4-carboxyphenylboronic acid is due to the formation of Pd(II) species, Pd nanoparticle leaching was studied for the supported catalysts in both reactions. The analysis of the Pd content of the recycled catalysts show that, after the consecutive catalytic cycles, a loss of ca. 22% of Pd was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-carboxy-rec** while a loss of ca. 25% was observed in **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50-vinyl-rec** (See Table S2 of supplementary material). These results confirm that, the differences in catalytic activity in the two studied reactions, are due to the formation of "Ar-Pd-OOC-Ar" (Pd(II) species) which decrease the halide conversion.

These materials show similar behavior to other analogous systems based on silica and described in the literature for the Heck reaction [44], and much higher recyclability than that reported for other hybrid materials used for other Suzuki-Miyaura C-C coupling reactions [24,29,45,46].

#### 4. Conclusions

We have synthesized and characterized a series of supported catalysts based on alumina and Pd-nanoparticles which are active in the Suzuki-Miyaura C–C coupling reaction observing good conversion rates in the reactions of 3-bromoanisole with 4-carboxyphenylboronic acid or 4-vinylphenylboronic acid. In general, **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50** with a higher amount of Pd gives higher conversion rates than **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20**, however, the TOF are lower in the case of **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50**, indicating a higher effectivity of the hybrid nanomaterial **nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20**. Furthermore, we have demonstrated the recyclability of the heterogeneous systems observing a loss of activity of the catalyst after the first recycle test of ca. 55% in the case of 4-carboxyphenylboronic acid and only 10% when using 4-vinylphenylboronic acid. The different behavior of the systems is most likely due the deactivation by a slight agglomeration of the Pd nanoparticles and in the case of the reaction with 4-carboxyphenylboronic acid the formation of stable intermediate species of the type "Ar-Pd-OOC-Ar" which may partially deactivate the Pd nanoparticles leading to lower conversions in the second and subsequent catalytic cycles.

#### 5. Acknowledgements

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### Tables, Schemes and Figures

Material	Starting Material (2.0 g)	Theoretical Pd content (%)	retical Pd Pd [PdCl <sub>2</sub> (cod)] tent (%) (mg) (mg)		Experimental Pd content (%)
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-1	nano-Al <sub>2</sub> O <sub>3</sub>	1	20 54		1.07
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-2	nano-Al <sub>2</sub> O3	2	40 108		2.05
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-5	nano- $AI_2O_3$	5	101 270		5.13
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-10	nano- $AI_2O_3$	10	201 540		8.54
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	nano- $AI_2O_3$	20	388 1040		9.25
nano-Al <sub>2</sub> O <sub>3</sub> -Pd-50	nano- $AI_2O_3$	50	1006 2700		21.40

Table 1. [PdCl<sub>2</sub>(cod)] quantities and Pd loading of the functionalization reactions on alumina

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**Table 2.** Specific surface area of alumina-based materials determined by  $N_2$ -adsorption-<br/>desorption isotherms

Table 3. Catalytic tests and quantification of 3-bromoanisole conversion at different reaction times for nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20

Catalytic test	Catalyst	Boronic acid	Time	Br conversion (%)	TOF (h <sup>-1</sup> ) <sup>a</sup> (Br conversion)
1	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	4-carboxy	0	0	0
			1	45±1	7.0±0.2
			2	61±2	4.8±0.2
			4	62±1	2.4±0.1
			24	65±1	0.4±0.1
			48	67±1	0.2±0.1
2	$nano\text{-}Al_2O_3\text{-}Pd\text{-}20$	4-vinyl	0	0	0
			1	16±2	2.5±0.3
			2	35±1	2.7±0.1
			4	41±1	1.6±0.1
			24	42 <u>+</u> 2	0.3±0.1
			48	45±1	0.1±0.1
0					

Table 4. Results of the catalytic tests and quantification of 3-bromoanisole conversion after 48 husing different quantities of nano-Al2O3-Pd-20 and nano-Al2O3-Pd-50

Catalytic test	Catalyst	Phenylboronic acid	mg of catalyst	Br conversion (%)	TOF (h <sup>-1</sup> ) <sup>a</sup> (Br conversion)
3	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	4-carboxy	15	72±1	4.6±0.1·10 <sup>-2</sup>
4	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	4-vinyl	15	77±1	4.9±0.1·10 <sup>-2</sup>
5	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-50	4-carboxy	15	95±1	2.6±0.1·10 <sup>-2</sup>
6	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-50	4-vinyl	15	94±2	2.6±0.1·10 <sup>-2</sup>
7	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	4-carboxy	5	32±2	6.1±0.4·10 <sup>-2</sup>
8	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-20	4-vinyl	5	40±1	7.7±0.2·10 <sup>-2</sup>
9	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-50	4-carboxy	5	46±2	3.8±0.2·10 <sup>-2</sup>
10	nano-Al <sub>2</sub> O <sub>3</sub> -Pd-50	4-vinyl	5	51±1	4.2±0.1·10 <sup>-2</sup>
11	[PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	4-carboxy	15	98±1	$\begin{array}{c} 0.9 \pm 0.1 \cdot 10^{-2} \\ (5.7 \pm 0.1 \cdot 10^{-2}) \end{array}$
12	[PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	4-vinyl	15	98±1	0.9±0.1·10 <sup>-2</sup> (5.7±0.1·10 <sup>-2</sup> )
13	[PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	4-carboxy	5	93±1	2.5±0.1·10 <sup>-2</sup> (16.3±0.1·10 <sup>-2</sup> )
14	[PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	4-vinyl	5	94±1	$\frac{2.5\pm0.1\cdot10^{-2}}{(16.5\pm0.1\cdot10^{-2})}$

<sup>a</sup> TOF refers to mol of Pd. For [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] data in brackets refer to mol of catalyst.

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Scheme 1. Catalytic reaction between 3-bromoanisole and 4-carboxyphenylboronic acid



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Scheme 2. Catalytic reaction between 3-bromoanisole and 4-vinylphenylboronic acid



**Figure 1.** C- and H-labeling for the product of the reaction between 3-bromoanisole and 4-vinylphenylboronic acid



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Figure 2. Nitrogen adsorption-desorption isotherms of a)  $nano-Al_2O_3-Pd-20$  and b)  $nano-Al_2O_3-Pd-50$ 



Figure 3. TEM images of Pd-functionalized materials a) nano-Al<sub>2</sub>O<sub>3</sub>-Pd-20 and b) nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50 after 48 h of reaction.



Figure 4. Results of the recyclability tests using the catalyst nano-Al<sub>2</sub>O<sub>3</sub>-Pd-50



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**Pd-supported nanoparticles** Heterogeneous catalysts for C-C coupling

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# Synthesis and study of the catalytic applications in C-C coupling reactions of hybrid nanosystems based on alumina and palladium nanoparticles

Abul Monsur Showkot Hossain, Adriana Balbín, Roghayeh Sadeghi Erami, Sanjiv Prashar, Mariano Fajardo, and Santiago Gómez-Ruiz\*

### Highlights

- · Pd-nanoparticles have been supported onto alumina-based nanomaterials
- Hybrid Pd-alumina materials have been characterized by different methods
- The catalytic activity of the hybrid materials has been tested in C-C coupling
- · Catalytic tests have been carried out studying the Pd loading influence
- Hybrid materials show a good degree of recyclability in consecutive catalytic tests