# Influence of the acidity of oxidized Pd/silica-alumina catalysts on their performances in the Suzuki coupling

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## Highlights

Oxidized Pd on Silica-Alumina catalysts are active and selective for the Suzuki coupling

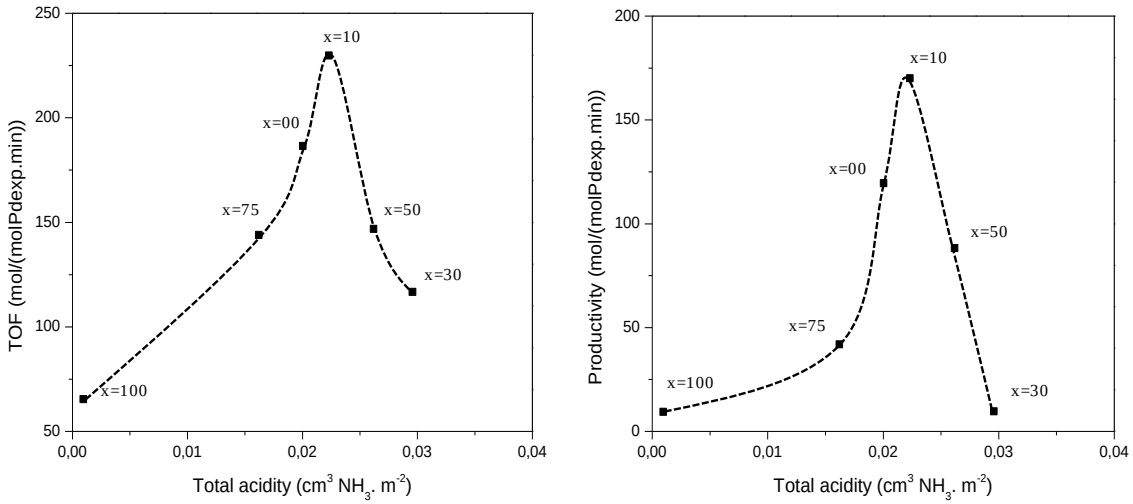
No leaching is observed and the catalysts are still efficient after 3 runs

TOF and productivity are optimized for a support containing 10% of silica

Optimum of performances is obtained with the most acidic catalyst

The importance of the support acidity in the Suzuki coupling is demonstrated

## Graphical abstract




Oxidized Pd supported on Silica-Alumina solid catalysts show optimum performances (TOF and productivity) in the Suzuki coupling when their content in silica (x) is 10%, which corresponds to the formulation with the highest acidity.

## Abstract

Suzuki coupling is a crucial reaction for the preparation of many high value compounds, especially for the synthesis of pharmaceuticals. Pd-based heterogeneous catalysts are highly regarded for achieving this reaction. However, the knowledge of the Suzuki mechanism with this type of catalysts is relatively limited. In the present paper, the influence of the acidity of heterogeneous catalysts on the Suzuki coupling has been methodically investigated on palladium supported on silica-alumina. A Suzuki coupling model reaction was used to assess if any correlation exists between the performances of the prepared catalysts and their acidity. The results have demonstrated that, the Pd being in an oxidized state, the acid sites at the heterogeneous catalyst surface participate actively to the mechanism of the Suzuki coupling. An optimum of total acidity of the catalysts leading to a peak of performances (conversion and selectivity) was identified. Several assumptions concerning the implication of the catalytic support in the different steps of the Suzuki coupling mechanism are proposed and discussed. Furthermore, the recyclability of the catalyst has been demonstrated, revealing that our catalysts really behave heterogeneously.

## Keywords

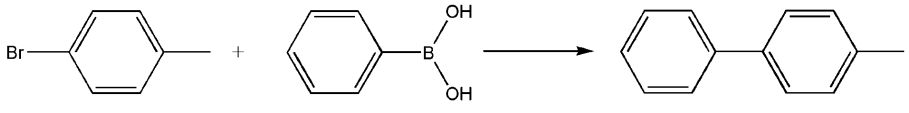
Suzuki coupling; heterogeneous catalysts; oxidized Pd/silica-alumina; acidity

# 1. Introduction

Chemical reactions aiming at the coupling of carbon atoms are important methodologies for the preparation of various organic molecules. In particular the Suzuki reaction is one of the most popular C-C coupling reactions [1]. This reaction was published at first in 1979 by Pr. Akira Suzuki [2] who obtained the 2011 Nobel Prize in Chemistry. Suzuki reaction is often a crucial step in the preparation of many compounds, especially in the synthesis of pharmaceuticals but also of materials such as liquid crystals [3, 4], organic conductive materials and semi-conductors [5].

The Suzuki reaction allows the combination of aryl halides ($Ar^1$-X) with aryl boronic acids ($Ar^2$-$B(OH)_2$) to form biaryls ($Ar^1$-$Ar^2$) (Eq. (1)) in the presence of a base [6]. This reaction is traditionally carried out with homogeneous catalysts. Soluble complexes of palladium generally associated to ligands of monoarylphosphine type such as the $Pd(PPh_3)_4$ [7, 8] are typically used but a large number of alternative homogeneous catalysts can be found in the literature [9-11]. The formation of carbon-carbon bonds with homogeneous catalysts has a high potential. Unfortunately these soluble complexes of palladium suffer from important downsides: (i) difficulties to recover them therefore to reuse them, (ii) contamination of the product with Pd and (iii) high cost. Furthermore, Suzuki reaction with homogeneous catalysts is only conducted in a batch reactor. This synthesis process generally implies a relatively long contact time between the catalyst and the reactants. This residence time in the reactor may conduct to consecutive reaction inducing a loss of selectivity to the desired product. Therefore, organic chemical industry is gradually turning towards reusable and cheaper heterogeneous catalysts for the economic and efficient use of raw materials eventually in continuous reactors.

$$Ar^1 - X + Ar^2 - B(OH)_2 \xrightarrow[Base]{Pd} Ar^1 - Ar^2 + B(OH)_2 X \quad (1)$$




4-bromotoluene Phenylboronic acid 4-methylbiphenyl (2)

The most common heterogeneous catalyst used for the Suzuki reaction is palladium supported on activated carbon (Pd/C) [1, 11]. Other supports are also reported in the literature including polymers [12-16], and also oxides like zeolites, MgO, $Al_2O_3$, $SiO_2$ … [6, 17-20].

Based on the accepted mechanism in homogeneous catalysis [5, 11, 21], Suzuki reaction requires the action of a base. This is true also for the heterogeneous process in which a base (typically $K_2CO_3$) must be added to the system [1, 22]. Furthermore one of the reactants is an acid (boronic acid, Figure 1). In the heterogeneous reaction, all reactants (acids and bases) have first to interact with the catalyst surface. Namely, the adsorption of all the reactants at the catalyst surface is a crucial and necessary step that must be optimized, or at least be taken into account. Understanding the acido-basic phenomena that govern the heterogeneous reaction, not only the adsorption, but also the chemical reaction itself, thus appears of upmost importance in the search for optimized catalytic formulations. The hypothesis that we want to challenge in the present paper is that the acido-basic properties of the supports should influence the catalytic activity. In other words it is explored here whether the balance of the acid, and basic, characteristics of the catalysts does indeed play a role on the adsorption step of the reactants and of the base, and consequently affects the activity of the Suzuki reaction.

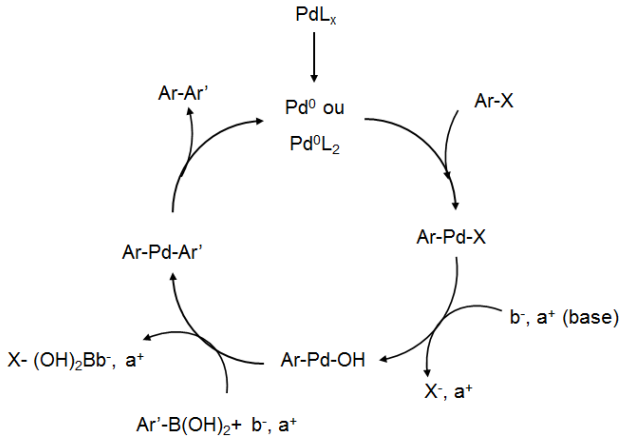



**Figure 1 : Suzuki mechanism in homogeneous catalysis (adapted from [5])**

In the present paper, the influence of the catalyst acidity on the Suzuki coupling has thus been systematically investigated on palladium supported on silica-alumina. The silica-alumina has an enormous significance as catalyst support in a broad range of chemical reactions, like in metathesis ($MoO_3/SiO_2$-$Al_2O_3$) [23, 24] and ammoxidation ($V_2O_5$-$MoO_3$-$P_2O_5/SiO_2$-$Al_2O_3$) [25]. Pd/$SiO_2$-$Al_2O_3$ formulations are also well recognized hydrogenation catalysts [26] and methanol synthesis [27].

The family of silica-alumina supports has been chosen here because their acid properties evolve quite regularly with the Si/Al ratio [28]. Pd catalysts supported on a series of silica-alumina with different Si/Al ratios have thus been prepared and characterized in terms of texture, compositions (bulk and surface), crystallinity and acidity.

A model reaction of the Suzuki coupling (Eq. (2)) has been used to evaluate the performances of the prepared catalysts and to establish the correlation between the catalyst acidity and their performances in the Suzuki reaction.

## 2. Experimental

2.1. Preparation of the supports and catalysts

Supports have been prepared by co-precipitation through hydrolysis of tetraethylorthosilicate (TEOS) and aluminium isopropoxide as described by Rouxhet and co-workers [29, 30]. The supports are denoted SA*x* where "*x*" represents the silica weight content in % and ranges from 0 to 100 %. Prior to wet impregnation, the supports were calcined at 500 °C for 15 h under static air.

Catalysts have been prepared by using a wet impregnation technique. The palladium is loaded on the oxide supports in a quantity of 5% in weight. 0.5212 g of the Pd precursor, tetraammine palladium chloride monohydrate ($Pd(NH_3)_4Cl_2.H_2O$, Aldrich, ≥ 99.99%), was dissolved in distilled water and the pH was adjusted to 10.6 with ammonia (Fisher Scientific, 35 wt.% in aqueous solution). 4g of calcined support was mixed with the solution for 1 hour under magnetic stirring. Water was then evaporated under reduced pressure in a rotavapor at 40 °C. The recovered solid was dried in air for one night at 110 °C and calcined at 500 °C for 3 h in a muffle furnace under static air. Catalysts were denoted Pd/SA*x*.

## 2.2. Characterization

The chemical composition of the supports and catalysts (Si, Al and Pd) was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) on an Iris Advantage equipment from Jarrel Ash Corporation.

Textural analysis of the samples was carried out on a Micromeritics Tristar 3000 apparatus using $N_2$ adsorption/desorption at liquid $N_2$ temperature, working with $P/P_0$ pressures in the range of $10^{-2}$ to 1. Before the measurements, 150mg of the samples were degassed at 150 °C overnight under vacuum (2 Pa). BET and BJH equations were used to determine the specific surface area, the porous volume and the pore size distribution.

Pd dispersion was determined via carbon monoxide chemisorption. These measurements were conducted at 35 °C using a Micromeritics Pulse Chemisorb 2700

apparatus equipped with a TCD detector. The samples (150 mg) were reduced at 300°C under a flow of pure hydrogen (Praxair, 99.995%) for 2 h, then flushed for 1 h under He (Praxair, 99.9997%) and finally cooled down to 35 °C. Several pulses of a known volume of CO (185 µl) were admitted sequentially. The metallic dispersion was calculated from the cumulative amount of adsorbed CO (i.e., the sum of nondetected CO in each pulse) as follows:

$$D = \frac{V_T.M}{V_M.m.C.L}$$

where $D$ is the metallic dispersion (%), $V_T$ is the total volume of adsorbed CO under normal temperature and pressure conditions, $M$ is the atomic weight of the metal (here Pd = 106.42 $g.mol^{-1}$), $V_M$ is the molar volume (22.414 $l.mol^{-1}$) of the active gas at normal conditions (0 °C, 1 atm), $m$ is the sample mass, $C$ is the CO adsorption stoichiometry coefficient on Pd (one adsorbed CO molecule per atom of Pd) [31, 32] and $L$ is the wt.% of the metal (here Pd) in the sample.

Surface characterization was performed by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra spectrometer (Kratos Analytical –Manchester – UK) equipped with a monochromatised aluminium X-ray source (powered at 10 mA and 15 kV). The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The pressure in the analysis chamber was around $10^{-6}$ Pa. The analyzed area was 700 µm × 300 µm. The pass energy of the hemispherical analyser was set at 160 eV for the wide scan and 40 eV for narrow scans. Charge stabilisation was achieved by using the Kratos Axis device. The electron source was operated at a filament current of 1.8 A and a bias of −1.1 eV. The charge balance plate was set at –2.9 V. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Si 2p, Al 2p, Pd 3d and C 1s again to check the stability of charge compensation in function of time and the absence of degradation of the samples during the analyses. Molar fractions (%) were calculated using peak areas normalized on the basis of acquisition parameters, sensitivity and transmission factors provided by the manufacturer.

X-ray diffraction (XRD) analyses were performed on the supports and catalysts on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The 2θ range was scanned between 5° and 90° at a rate of 0.02°.$s^{-1}$. Identification of the phases was carried out using the ICDD-JCPDS database.

The acidity of the samples has been evaluated by $NH_3$-chemisorption on a Micromeritics ASAP2010 Chemi equipment, as described in reference [28]. The U-shaped sample tube containing 150 mg of the catalyst was first flushed under a He (Praxair, 99.9997%) flow at 300 °C for 2 h and then evacuated for 2 h down to a residual pressure (<0.67 Pa). A first $NH_3$ adsorption isotherm was recorded at 50 °C. Then the sample was evacuated for 2 h down to a residual pressure (<0.67 Pa) at the same temperature and a second $NH_3$ adsorption isotherm was measured. The difference between the two isotherms corresponds to the amount of ammonia chemisorbed on the samples at 50 °C. The intercept of a linear interpolation built on the difference points measured between 200 and 700 mmHg is taken as a measure of the acidity of the samples. The results are expressed in terms of $cm^3$ of chemisorbed $NH_3$ (STP) per gram of catalyst. The values are also normalized by the surface specific area of the sample.

## 2.3. Typical reaction procedure

The probe reaction used in this paper concerned the synthesis of biaryl molecules by the coupling of aromatic carbons (Suzuki reaction, Eq. (2)). The reactants were the 4-bromotoluene (Merck, 98%) and the phenylboronic acid (Merck, f.a.). The desired product was the 4-methylbiphenyl. The reaction was carried out in the presence of $K_2CO_3$ (Merck, f.a.) as required base.

All catalysts were sieved and selected in the 100-200 µm granulometric fraction. The catalytic tests were carried out in a round flask with mechanical agitation (210 rpm). The solid reagents, 4-bromotoluene (3.0784 g, 0.15 $mol.l^{-1}$) and phenylboronic acid (3.2921 g, 0.225 $mol.l^{-1}$), the catalyst 0.1000 g and the internal standard, namely biphenyl, (2.2206 g, 0.12 $mol.l^{-1}$) were introduced first, followed by the solvent, 120 ml of dimethylformamide (DMF). The reactor was placed in a thermostated oil bath and the reaction was performed under a nitrogen atmosphere. The reaction temperature was 65 °C. The reaction began when 30 ml of the aqueous solution of $K_2CO_3$ (0.15 $mol.l^{-1}$) was added (t = 0 min). Samples (0.5 ml) of the reaction medium were taken every 5 min after adding the base until 30 min and then two additional aliquots were taken at 45 and 60 min. Before analysis, samples are filtered (PTFE syringe filters, filtration threshold 0.45 µm) to remove the catalyst. For the analysis, the samples were diluted (1:9 vol) in dichloromethane (Merck, ≥99.9%) and analyzed by a CP-3800 gas chromatograph (GC) from Varian equipped with a FID detector and an autosampler (CP-8200 Varian) on a column CP-Sil 5CB (50 m x 0.32 mm x 0.4 µm).

The conversion is defined as the ratio "(number of moles of 4-bromotoluene converted/mole of 4-bromotoluene initial) * 100 %". The selectivity for the 4-methylbiphenyl is defined as the ratio "(number of moles of 4-methylbiphenyl produced/mole of 4-bromotoluene consumed) * 100 %". To better compare the catalyst, the TOF ("Turn-Over Frequency") has been used. This value represents the number of moles of 4-bromotoluene converted per mole of Pd exposed at the surface of the catalyst (using the dispersion of Pd determined by CO chemisorption) and per minute. A productivity of the 4-methylbiphenyl can be also defined as follows: "TOF x Selectivity of 4-methylbiphenyl". This value has also been calculated after 5 min of reaction to have the initial rate of the reaction.

2.4. Catalyst recyclability

After a run under the typical reaction conditions described above, the solid was filtered and washed 5 times with DMF to remove the organic substrates and 5 times with water to remove the base. Then the solid was dried at 110 °C. The recovered catalyst was weighted and a reaction was run using proportional amounts of solvent and reactants to the recovered catalyst amount to maintain the same reactants/catalyst ratio. Three complete cycles have been performed for the Pd/SA10 catalyst.

The recovered liquid medium (LM) from the filtration was kept in the reaction conditions and samples were analysed periodically. The LM was also analysed by ICP-AES in order to detect the eventual leached species.

## 3. Results

3.1. Supports and catalysts characterizations

The Si content in the bulk of the supports has been checked by ICP-AES. The surface composition of the prepared supports has been measured by XPS. The results show that the experimental composition of the bulk and the surface are close to the theoretical one (Figure 2).

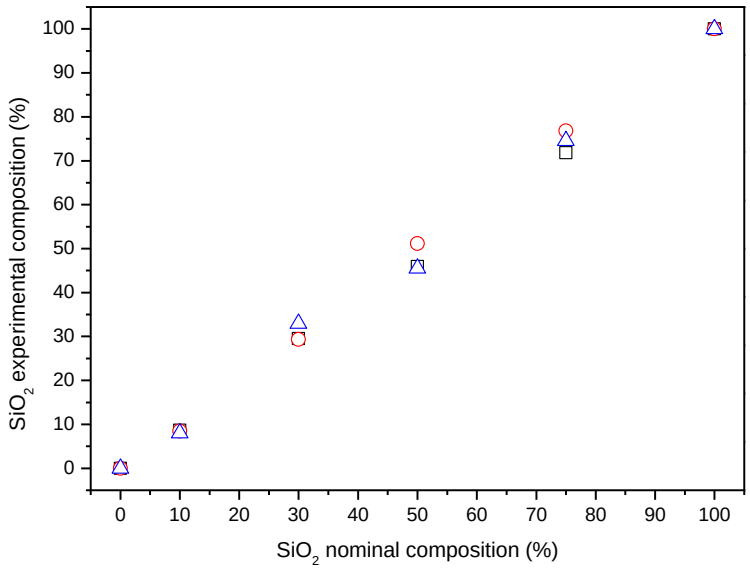



**Figure 2: $SiO_2$ content in the support as determined (□) from the theoretical composition, (○) from ICP-AES and (Δ) from XPS measurements.**

Table 1 presents the textural properties evaluated by $N_2$-physisorption. The specific surface area (SSA) of the supports increases from pure alumina (SA00) to SA30 and decreases from SA30 to SA75. The highest SSA value is obtained for the pure silica SA100 (429 $m^2.g^{-1}$). The same tendency is observed for the pore volume. After the impregnation of Pd, the SSA and the pore volume decrease slightly.

**Table 1: Specific surface area, pore volume and pore diameter of the supports and the catalysts; Pd content and dispersion of the catalysts**

| Supports or catalysts | SSA ($m^2.g^{-1}$) | Pore V ($cm^3.g^{-1}$) | Pore D (nm) | Pd content (wt. %) | Pd dispersion (%) |
|---|---|---|---|---|---|
| SA00 | 211 | 0.52 | 7.2 | - | - |
| Pd/SA00 | 172 | 0.43 | 7.3 | 5.0 | 18 |
| SA10 | 316 | 0.78 | 7.0 | - | - |
| Pd/SA10 | 272 | 0.70 | 7.1 | 4.8 | 10 |
| SA30 | 340 | 0.88 | 7.4 | - | - |
| Pd/SA30 | 318 | 0.83 | 7.6 | 4.7 | 7 |

| | | | | | |
|---|---|---|---|---|---|
| SA50 | 200 | 0.90 | 15.0 | - | - |
| Pd/SA50 | 176 | 0.84 | 15.7 | 4.9 | 6 |
| SA75 | 152 | 0.71 | 17.5 | - | - |
| Pd/SA75 | 130 | 0.66 | 18.2 | 5.0 | 4 |
| SA100 | 481 | 1.05 | 8.8 | - | - |
| Pd/SA100 | 429 | 0.93 | 7.1 | 4.9 | 3 |

The Pd content of each catalyst has been checked by ICP-AES. For all of them, these values are in excellent agreement with the theoretical loading (5 wt. %) whatever the support composition (Table 1). Pd dispersion on the other hand, is highly affected by the composition of the support. Pd is better dispersed when the material contains more Al. In other words, the mean palladium particles size is expected to be smaller in the samples with lower silica content.

The XPS Pd/(Si+Al) atomic ratio gives an idea of the quantity of Pd on the external surface of the catalysts (Figure 3). It has observed that this ratio depends on the composition of the supports. In fact from SA00 to SA50, Pd/(Si+Al) decreases and from SA50 to SA100, it increases: a minimum of Pd/(Si+Al) is thus found for SA50. Depending on the composition of the support (i.e. its ratio Si to Al), the binding energy at which the Pd 3d5/2 peak appears varies in the range 336.1 – 337.2 eV. This clearly excludes the possibility that the Pd at the surface of our catalysts is in the metallic state (Pt°). Metallic Pd species would have induced a Pd 3d5/2 contribution at about 335 eV, which we did not detect [33]. The presence of a Pd contribution as in the range of binding energy found here indicates that Pd is in an oxidized state. Whereas $Pd^{4+}$ presents its 3d5/2 peak around 337 eV, and $Pd^{2+}$ presents it close to 336 eV, it has also been found that the precise position of this peak depends on the particle size, with a progressive shift towards higher binding energies when the size decreases. It is thus not

possible to further precise whether the Pd species in our catalysts are in the 2+ or in the 4+ state. Further details about energy scale calibration and identification of palladium oxidation state is largely described in [34, 35].

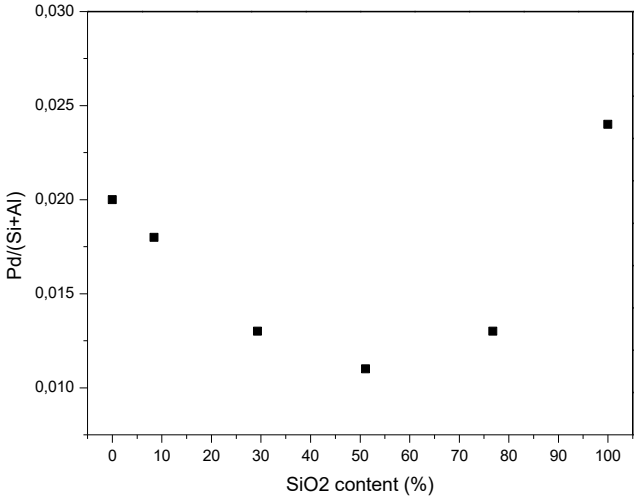



**Figure 3: Pd/(Si+Al) atomic ratio measured by XPS for each prepared catalysts.**

In XRD experiments, a large band around 20-25° appears for the samples with a high $SiO_2$ content. This band is typical of amorphous materials and shifts towards higher 2θ values with lower contents of $SiO_2$. The peaks at 2θ = 19.5°, 31.9°, 37.6°, 45.9° and 67.0° are characteristic of crystalline alumina and appears only above 70% of $Al_2O_3$. These peaks get narrower as the Si/Al ratio decreases. The nature of this alumina could not be accurately determined; the peaks may either correspond to γ-$Al_2O_3$ (JCPDS 29-0063) or to δ-$Al_2O_3$ (JCPDS 46-1131). Besides, diffractograms of the catalysts (Fig. 4) are similar and peaks of crystalline PdO (Palladinite) (JCPDS 41-1107) (2θ (h, k, l) = 33.8° (1 0 1), 54.7° (1 1 2), 60.3° (1 0 3)) are systematically observed.

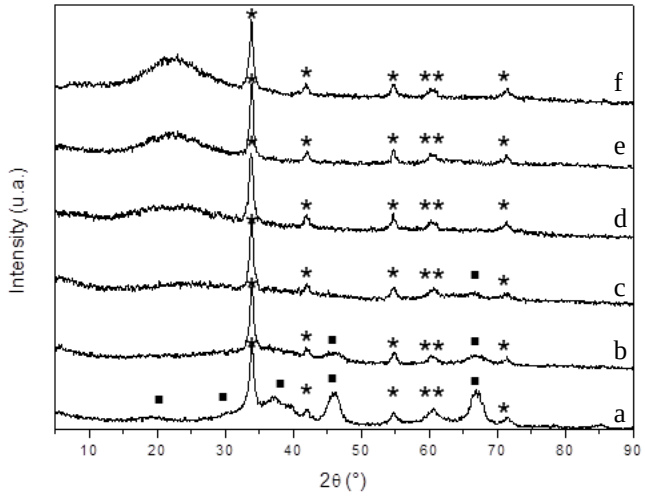



**Figure 4: XRD patterns of the catalysts: (a) Pd/SA00, (b) Pd/SA10, (c) Pd/SA30, (d) Pd/SA50, (e) Pd/SA75 and (f) Pd/SA100. Peaks correspond to (■) alumina and (*) PdO.**

The total acidity of the supports and catalysts was evaluated by $NH_3$-chemisorption. The results are expressed in terms of the amount of ammonia chemisorbed normalized by the surface specific area (Figure 5). The total surface acidity of the samples is clearly dependant on the support composition. It appears that the pure silica support (SA100) only presents a small number of acid sites. It is well-known indeed that the silica-alumina materials have more numerous acid sites than silica [29, 30, 36]. From pure alumina (SA00) to SA30, an increase in the number of acid sites is observed and from SA30 to pure silica, a decrease is observed. This trend is valid for the supports but also for the catalysts. As a general rule, the impregnation of Pd onto the supports however induces a decrease of the total acidity of the latter.

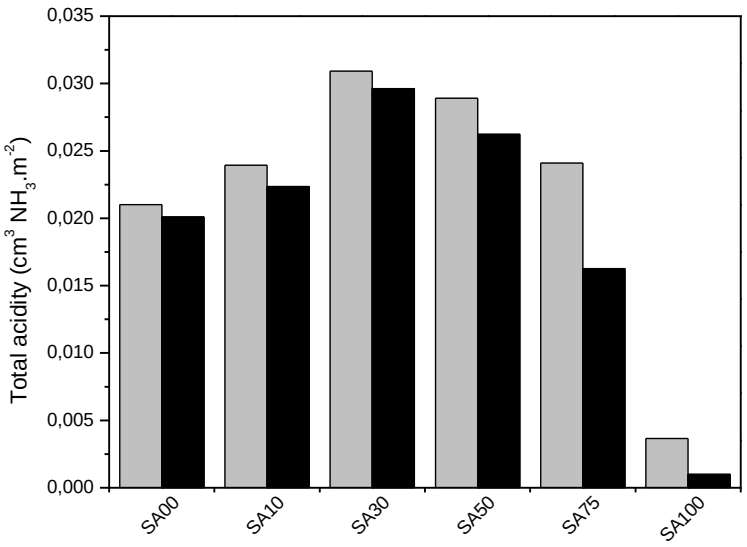



**Figure 5: Total acidity of the supports (grey columns) and the catalysts (black columns)**

## 3.2. Catalytic activity

A Suzuki model reaction has been used to determine the activity of the Pd/SA*x* catalysts. In this reaction, 4-bromotoluene reacts with the phenylboronic acid (Eq.(2)). Blank tests have been conducted to determine if the reaction could be carried out (i) without any solids and (ii) with the supports only (no Pd). In all cases, no conversion at all was observed after 60 minutes of test. So, the performances measured with our catalysts may unambiguously be attributed to the presence of Pd. Figure 6 represents a typical evolution of the conversion of the 4-bromotoluene and the selectivity to 4-methylbiphenyl which is the only product detected. The selectivity is however lower than 100%, closing a value of 90%. Several assumptions can explain this. Firstly, an irreversible adsorption of the reagents and/or of the desired product (4-methylbiphenyl) could happen at the surface of the catalysts. Secondly, it is possible that another product than the 4-methylbiphenyl is produced during the reaction and that it would remain strongly adsorbed on the catalysts and/or would not be detected by gas chromatography due to its low volatility.

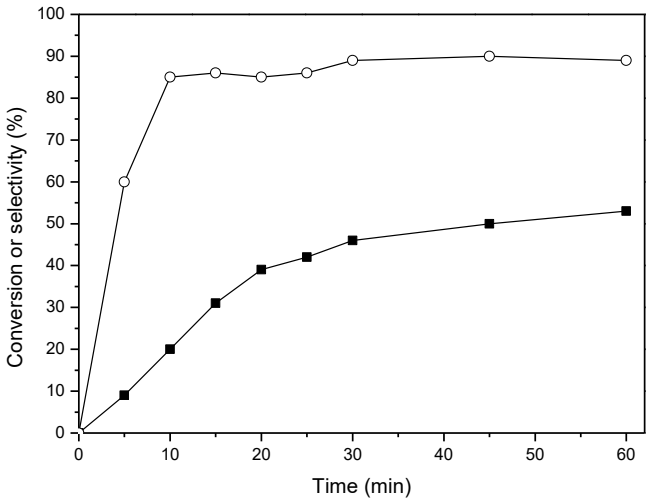



**Figure 6: Evolution of (■) the conversion of 4-bromotoluene and (○) the selectivity of the desired product (4-methylbiphenyl) obtained with Pd/SA50 catalyst.**

The catalysts performances have been normalized to take into account the differences of loading and dispersion of the palladium on the different samples. The conversions are thus expressed in terms of "turn over frequency" (TOF) (Table 2). These values have been calculated after 5 minutes and are considered to represent the initial rate of the reaction. Table 2 shows also the selectivity and the productivity of 4-methylbiphenyl after 5 min of reaction. It is difficult to compare these productivity values with those from previous publications as [17, 18] as these do not mention unambiguously the dispersion of the Pd in the corresponding catalysts, and as the conditions used in the respective studies are different. However, taking into the lower temperature and the smaller mass of Pd used in our study, it sounds that the performance observed here are superior, in particular at the beginning of the tests; which makes our catalysts much promising for achieving the Suzuki-Miyura reaction, for example in a continuous process.

**Table 2 : Turn over frequency (TOF), selectivity of 4-methylbiphenyl and productivity calculated after 5 minutes of reaction for all the catalysts**

| | Pd/SA00 | Pd/SA10 | Pd/SA30 | Pd/SA50 | Pd/SA75 | Pd/SA100 |
|---|---|---|---|---|---|---|
| TOF[1] | 186 | 229 | 116 | 147 | 143 | 65 |
| Selectivity (%) | 64 | 74 | 8 | 60 | 29 | 14 |
| Productivity[2] | 119 | 169 | 9 | 88 | 41 | 9 |

[1]($mol_{4\text{-bromotoluene}}.mol_{Pdexp}^{-1}.min^{-1}$); [2]($mol_{4\text{-methylbiphenyl}}.mol_{Pdexp}^{-1}.min^{-1}$)

The calculated TOF and the productivity (Table 2) have been compared to the total acidity measured by $NH_3$-chemisorption (respectively Figures 8a and 8b): an optimum of total acidity of the catalysts is found corresponding to Pd/SA10. This optimum may be also found when comparing the selectivity and total acidity (not shown).

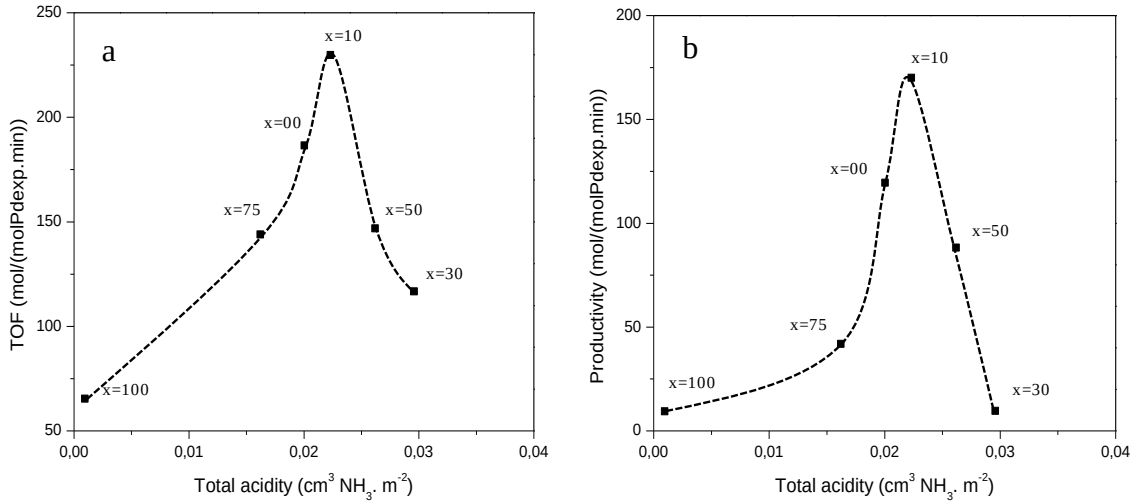



**Figure 8: Evolution of (a) the TOF and (b) the productivity with the total acidity of the catalysts. "x" represents the % of $SiO_2$ in the supports.**

## 3.3. Recyclability of the catalysts

The catalysts have been washed with DMF and water and reused 3 times to test their recyclability. The recovered catalyst was weighted and the reaction was run using solvent and

reactants in proportional amounts to maintain the same reactants/catalyst ratio. As an example, Table 3 presents the results obtained for Pd/SA10. The catalyst appears recyclable, as no loss of TOF, selectivity and productivity is observed. This observation is valid for all the catalysts.

**Table 3: Recyclability of the Pd/SA10 catalyst**

| | TOF (mol/($mol_{Pdexp}$.min) | Selectivity (%) | Productivity (mol/($mol_{Pdexp}$.min) |
|---|---|---|---|
| Pd/SA10 1st run | 229 | 74 | 169 |
| Pd/SA10 2nd run | 227 | 71 | 162 |
| Pd/SA10 3rd run | 235 | 71 | 167 |

The recovered liquid medium (LM) from the filtration of the catalyst (Pd/SA10) was kept in the reaction conditions and samples were analysed periodically. The conversion and the selectivity do not increase anymore. The LM was also analysed by ICP-AES in order to detect the eventual leached species. No trace of Pd or of the support constituents was detected.

## 4. Discussion

### 4.1. Supports and catalysts characterizations

The chemical compositions of the bulk and the surface of the supports are close to the nominal composition calculated from the amounts of reagents used for their preparation. This indicates that the parameters of the supports synthesis have been well controlled and allows considering that the composition is homogeneous in the whole sample (bulk and surface).

The specific surface area (SSA) developed by the supports depends of their $SiO_2$ content. The SSA decreases from SA30 to SA75. A hypothesis has been proposed by Rouxhet et *al.* [37] to explain this observation: a weakly polymerized alumina in the fresh gel would

appear during the support synthesis, affecting the coagulation of the colloidal particles, and would consequently influence the support SSA.

As expected (due to the use of wet impregnation), the Pd loading for all the catalysts is close to the nominal one. The SSA as well as the pore volume decrease after the impregnation of the palladium on the supports. This may be due to the formation Pd particles plugging partially the pores or by a partial degradation of the material structure due to the pH (10.6) of the synthesis of the catalysts.

The $SiO_2$ content in the Pd/SA*x* catalysts affects the Pd dispersion in the catalysts. It is observed that the Pd dispersion decreases with increasing $SiO_2$ content in the Pd/SA*x* catalysts. In other words, palladium spreads better in the presence of alumina. This can be explained by the assumption that the interaction between the metal and $SiO_2$ is lower than that between metal and $Al_2O_3$ [38, 39]. An increase in the $SiO_2$ content in the Pd/SA*x* catalysts seems to cause a decrease of interaction between Pd and SA*x* support, leading to the aggregation of Pd and consequently to a lower Pd dispersion. This indicates that $Al_2O_3$-rich supports are more indicated for obtaining high Pd dispersion in Pd/SA*x* catalysts.

The atomic Pd/(Si+Al) ratio measured in XPS also depends strongly on the composition of the supports. A U-shaped curve was observed with a minimum for the SA50 support. The variation of the Pd/(Si+Al) atomic ratio is not due to modification of the Pd dispersion. Indeed, the Pd dispersions and the Pd/(Si/Al) ratios do not evolve in the same way. So, the explanation of this U-shaped curve for the Pd/(Si+Al) atomic ratio rather comes from the fact that the palladium goes deeper into the pores of the Pd/SA50 catalyst likely because SA50 has a higher pore diameter.

The X-ray diffraction patterns of the supported catalysts show well-defined and intense peaks corresponding to the presence of crystalline PdO. These peaks confirm that the oxidation state of the palladium is +2, as expected. The diffractograms also show that the

supports are practically amorphous. Apart from the amorphous silica-alumina matrix, the onset of a crystalline $Al_2O_3$ phase is observed in the support with at least 70% alumina in the support.

$NH_3$-chemisorption measurements show that silica is barely acidic, while the pure alumina and the silica-aluminas show a much stronger total acidity. This increase was reported in the literature [30, 37] and is due to the formation of $SiAlO_x$ phase during the supports synthesis when the proportion of $Al_2O_3$ is comprised between 5 and 25 wt. %. This mixed-phase bears acidic hydroxyl groups attached both to a Si and an Al atom (Si–Al bridging hydroxyl groups, also written Si–OH–Al). The formation of these hydroxyl groups is the result of the substitution of $Si^{4+}$ by $Al^{3+}$ in a tetrahedral arrangement. However, when the proportion of $Al_2O_3$ is higher than 25 wt. %, a highly dispersed alumina phase appears at the expense of the mixed SiAlO*x* phase. In Figure 5, the acidity increases from pure silica (SA100) to SA30 due to the formation of $SiAlO_x$ phase and, from SA30 to pure alumina, the acidity decreases due to the onset of dispersed alumina.

## 4.2. Catalytic activity

Supports alone show no activity demonstrating that the only active species is the palladium. Furthermore, the catalysts are recyclable (Table 3), indicating that the palladium is not leached during the catalytic tests. This is confirmed by the elementary analyses (ICP-AES) of the liquid media.

Concerning the oxidation state of the active Pd species in heterogeneous catalysts, the literature is truly indecisive. Indeed, some authors [40, 41] argue that the Pd must be used in its metallic form ($Pd^0$) as for homogeneous catalysts (Figure 2). Others [1, 11] claim that it must be oxidized ($Pd^{2+}$) and a third group [1, 11] argues that the oxidation state of Pd has no

influence. Our catalytic tests support the conclusion that the reaction proceeds in the absence of $Pd^0$, suggesting that an oxidized Pd species is active. Dependence of the position of the $Pd^{n+}$ peaks in XPS with the particles size does not allow to further precise unambiguously whether the Pd state at the surface of our catalysts in 4+ or 2+.

Figure 9 shows the evolution of the TOF of 4-bromotoluene as a function of Pd dispersion. If the activity of the reaction depended only on Pd dispersion, a straight line with a slope of zero should be obtained on this Figure 9, as the TOF is expressed and thus already normalized by the number of Pd atoms exposed at the catalyst surface (measured by CO chemisorption). This is not the case. Clearly, the variability observed between the different catalysts cannot fully and directly explained by Pd dispersion.

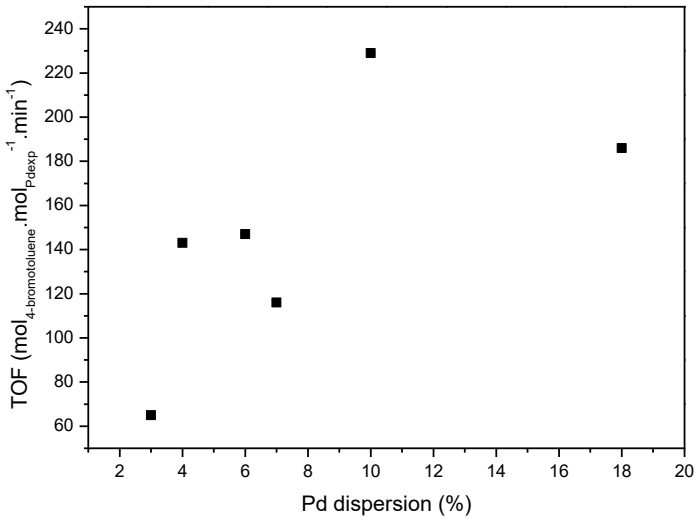



**Figure 9: Evolution of the TOF of the 4-bromotoluene as a function of Pd dispersion**

A correlation between the activity and the total acidity has been established. This indicates that the acido-basic properties of the catalysts are really involved in the catalytic behavior of the Suzuki reaction. First, these properties may be involved in the adsorption of the reagents, namely the 4-bromotoluene and phenylboronic acid. An acidity optimum could improve the adsorption of these reactants. On the one hand, if the catalyst is too acidic, the

adsorption will be irreversible and will inhibit the reaction. On the other hand, if the catalyst is not acidic enough the adsorption will be the limiting step of the reaction rate. Data plotted in Figures 8a and 8b depict well this situation.

The second assumption to explain how the catalysts acidity might modify the activity of the Suzuki coupling, is based on the reaction mechanism proposed in homogeneous catalysis. The base is involved at two levels: (i) the replacement of the halide ($X^-$) of the complex Ar-$Pd^{2+}$-X with a hydroxyl group ($OH^-$) to form the complex Ar-$Pd^{2+}$-OH and (ii) the activation of the phenylboronic acid (Figure 1). In the heterogeneous catalysis mechanism, it is possible that the surface OH groups of the catalysts participate in (one of) these steps.

The catalyst appears recyclable, as no loss of TOF or of productivity is observed after 3 runs. This indicates that Pd is not leached from the catalysts. So, it can be unambiguously said that we are in the presence of a real heterogeneous catalysis.

## 5. Conclusion

The influence of the acidity of silica-alumina supported Pd-catalysts with different $SiO_2$ content (between 0 and 100 wt. %) on their activity in the Suzuki reaction has been studied: the catalysts acidity strongly depends on the composition of the supports.

Results demonstrate that the an oxidized $Pd^{n+}$ species is essential to carry out the reaction and the palladium is not leached during the catalytic tests.

Correlations between the activity and the total acidity have been established: an optimum of total acidity of the supports and catalysts was found to improve the activity. The supports and catalysts could be involved at different stages of the reaction. The catalysts may be involved in the adsorption of the reagents. An acidity optimum could improve the adsorption of these reactants. On the one hand, if the catalyst is too acidic, the adsorption will

be irreversible and will inhibit the reaction. On the other hand, if the catalyst is not acidic enough the adsorption will be the limiting step of the reaction rate. Furthermore, a base is needed for the reaction and is involved at two levels: (i) the activation of the 4-bromotoluene and (ii) the activation of the phenylboronic acid. In the heterogeneous catalysis mecanism, it is possible that the surface OH groups of the catalysts participate in (one of) these steps.

Finally, the recyclability tests have demonstrated that we are in the presence of a real heterogeneous catalysis.

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