

# The Influence of the Nature of the Support on the Copper– Palladium Catalysed Suzuki–Miyaura-Coupling

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**Abstract** Copper–palladium bimetallic catalysts supported on mixed oxides  $(MgO)_{0.75}(Al_2O_3)_{0.25}$  (MgAlO) were prepared with two step impregnation (TSI) and co-impregnation (CI). These materials were studied to determine the effect of the support on the activity and stability in the Suzuki–Miyaura reaction and on the properties of a catalyst. The catalyst prepared by CI was active and selective during 6 catalytic cycles in Suzuki coupling, whereas the activity of the catalyst prepared with TSI dropped at the sixth use. The kinetics of the reaction was examined along with its scope. The relationship between the basic properties of the support and the catalytic performances were examined too. The importance of the nature of the support was also studied by catalyst characterization methods.

## **Graphical Abstract**

catalyst K<sub>2</sub>CO<sub>3</sub> ethanol



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## **1** Introduction

Heterogeneous catalysis has an important role in organic chemistry. 'In about 85–90 % of all chemical manufacturing processes use is made of a catalyst. Furthermore, in

about 80–85 % of all of those catalytic processes, heterogeneous catalysis is employed.' [1] Still the development and complete understanding of the catalytic cycle and catalytically active species in heterogeneous catalysis remain a challenge.

The Suzuki-Miyaura reaction is a well known tool for carbon-carbon bound formation [2]. It consists of the coupling of a halide with boronic acid in the presence of catalyst (mostly palladium), ligand if necessary and base. Since it was first reported in 1979 several attempts were made to carry out this coupling. The most challenges from green chemistry's point of view are the followings: the catalyst, which is preferably stable, recyclable and heterogeneous without the necessity of a ligand; and the selection of the base or the reduction of its quantity so that the reaction might be more atom efficient. The catalyst classically is palladium which can be either homogeneous [3-6] or heterogeneous [7–9]. Recently a coupling of hindered aryl chlorides with arylboronic acids in the presence of a mono-N-heterocyclic carbene palladium complex was reported [10]. The main part of publications concerns the homogeneous route whereas heterogeneous catalysts are preferable as it is easier to extract them from the reaction medium and to reuse/recycle/regenerate them. The heterogenisation of a homogeneous catalyst was described in a study where an N-heterocyclic carbene palladium complex was immobilised on chemically modified MCM-41 and the performances were tested in the Suzuki-Miyaura reaction [11]. Only a few examples concerning Cu-Pd bimetallic catalysts were published for this coupling [12-18]. As a homogeneous route Cu<sub>2</sub>O was proved to be a remarkable co-catalyst in the Pd(PPh<sub>3</sub>)<sub>4</sub> catalysed reaction of arylboronic acids with ethyl bromoacetate [12]. Furthermore a Suzuki-type C-H arylation of azoles was reported with Pd(OAc)<sub>2</sub>, Cu(OAc)<sub>2</sub> and CuCl [13]. The beneficial effect of the CuCl was described in the Pd(OAc)<sub>2</sub> catalysed Suzuki coupling of 2-heterocyclic boronates [14]. Liebeskind et al. reported a palladium catalysed copper mediated route for the coupling of aryl and alkenyl iodides and arylboronic acids in the absence of base and with copper(I) thiophene-2-carboxylate as mediator [15]. Using copper based support proved also to be suitable as Pd

Table 1 Properties of Cu-Pd-4A-TSI and Cu-Pd-4A-CI [34]

Property	Cu-Pd-4A-TSI	Cu-Pd-4A-CI
Quantity of Cu (wt%)	6.2	5.7
Quantity of Pd (wt%)	2.4	2.0
BET surface area (m <sup>2</sup> /g)	310	230
Pore volume $(cm^3/g)$	0.204	0.142
Pore diameter (Å)	26	25
Average particle size (nm)	2.5	2.2

nanoparticles supported on CuO were described as efficient catalyst for the reaction [16]. The application of copper nanoclusters and Cu/Pd nanoclusters have also been reported for this reaction [17, 18]. In a patent Pd/Cu colloids in different molar composition were examined and it was found that the Pd(50 %)/Cu(50 %) composition was the most efficient [19]. The common values for metal loadings in the literature for these reactions are 5 mol% Pd-salt and 10-100 mol% Cu-salt to perform the reaction. As for the conditions of the reaction the application of a base is necessary. The most frequently used bases for this coupling are NaOEt [2], NaOH [20, 21], KOH [22], K<sub>3</sub>PO<sub>4</sub> [23, 24], Cs<sub>2</sub>CO<sub>3</sub> [25], K<sub>2</sub>CO<sub>3</sub> [26–28], Na<sub>2</sub>CO<sub>3</sub> [29, 30]. Their quantity varied between 1.1 and 10 equivalents. However the Suzuki-type coupling has also been reported without a base [15, 31-33] but in this case the application of exotic reaction triarylantimony partners such as diacetates and tetra(alkoxo)diborons [31]; organo-antimony or -bismuth compounds [32] and hydroxy(tosyloxy)iodobenzene [33] were required.

Within our research group we study supported metal catalysis in organic reactions [34]. A copper-palladium catalyst was previously developed and tested in the Suzuki-Miyaura reaction [35, 36]. The catalysts were characterised, and their main properties are shown in Table 1. It was found that during wet impregnation the order of metal precursors' addition influenced the metalmetal interaction therefore the catalyst's stability in the Suzuki-Miyaura reaction. In the further experiments we wanted to study the effect of the support. In the previous experiments the support was 4A, an A zeolite. It has basic properties, its pH of the 5 % slurry is 10.5 [37] and it can adsorb water, thus it is commonly used as drying agent. We continued our study by a support which had stronger basic character. MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxides are widely used as solid bases [38, 39] and also as inorganic supports for transition metals [40-43]. Furthermore they showed promising properties in a previous study whereas the basic properties of the mixed oxides with different ratios were also reported [43, 44]. Taking into account the described observations our choice was MgO-Al<sub>2</sub>O<sub>3</sub> with 3:1 ratio as support to examine.

Since the nature of the catalytic support has influence on the particle size, pore size and structure, surface area and on its basic properties we have undertaken to determine the properties that have influence on the stability and kinetics of the Suzuki–Miyaura reaction. Furthermore our wish was to investigate if a catalyst with stronger basic properties might result in the elimination of the base used from our catalytic system as it will be interesting from an environmental point of view to avoid the treatment of the solvent used due contamination by the base. We investigated not only the catalytic activity and stability, but the catalyst characterization was also performed (ICP, BET, XRD, TEM, EDS, TPR and FT-IR).

## 2 Experimental

Iodobenzene ( $\geq 99 \%$ ) for synthesis and copper(II) chloride ( $\geq 99 \%$ ) for synthesis were purchased from Merck Ltd. Sodium tetrachloropalladate(II) (98 %), magnesium ethoxide (98 %), aluminium-tri-*sec*-butoxide (97 %) and phenylboronic acid (97 %) were purchased from Sigma-Aldrich Co. LLC.

## 2.1 Catalyst Preparation

# 2.1.1 Preparation of MgO-Al<sub>2</sub>O<sub>3</sub> Mixed Oxides with Sol-Gel Method

The composition of the prepared mixed oxides was  $(MgO)_{0.75}(Al_2O_3)_{0.25}$ .

In a 2-neck round bottom flask 0.1346 mol magnesium ethoxide in 134 ml ethanol was brought to reflux and was stirred for 15 min. After ~1 g of oxalic acid—dissolved in minimum amount of water (~10 ml)—was added to obtain pH 5. This mixture was stirred at reflux for 2.5 h. Then 0.08978 mol aluminium-tri-*sec*-butoxide and 162 ml water were added. This mixture was stirred for further 15 min at reflux. Then it was dried at 80 °C for a night and was continued to dry at 120 °C for 8 h. Then it was calcined under air with the following temperature profile: 5 °C/min until 250 °C, then 250 °C for 1 h, 5 °C/min until 600 °C, 600 °C for 3 h, 10 °C/min until 30 °C.

# 2.1.2 Preparation of Monometallic Catalysts with Wet Impregnation

To prepare the monometallic catalyst 1 g of powdered MgAlO  $[(MgO)_{0.75}(Al_2O_3)_{0.25}]$  was stirred with the corresponding metal precursor (1 mmol of anhydrous copper(II) chloride or 0.2 mmol of sodium tetrachloropalladate(II)) in 30 ml of deionised water at room temperature for 12 h. Then it was dried in sand bath at 120 °C for 5 h and calcined with the temperature profile described above. The targeted metal content of the catalyst thus obtained is 6.3 wt% copper (Cu–MgAlO) and 2.1 wt% palladium (Pd–MgAlO).

# 2.1.3 Preparation of Bimetallic Catalysts with Successive and Co-impregnation

Successive impregnation (TSI) consists in stirring the monometallic catalyst (Cu–MgAlO) previously prepared with sodium tetrachloropalladate(II) as described above.

In the co-impregnation method (CI), the two metal salts were added simultaneously to the suspension of MgAlO in deionised water. The thermal treatments were the same as described above. The targeted Pd/Cu molar ratio was 0.2:1 in both cases.

# 2.2 Typical Procedure for the Suzuki–Miyaura-Coupling

An Agilent 6890 N-GC-5973 N-MSD chromatograph, using a 30 m  $\times$  0.25 mm Restek, Rtx-5SILMS column with a film layer of 0.25  $\mu$ m was used for GC–MS measurements. The temperature of the injector was 250 °C. The initial temperature of column was 45 °C for 1 min, followed by programming at 10 °C/min up to 310 °C and a final period at 310 °C (isothermal) for 17 min. The carrier gas was He and the operation mode was splitless.

<sup>1</sup>H NMR spectra were made on BRUKER Avance-300 instrument using TMS as internal standard in CDCl<sub>3</sub>.

Before the reaction, the catalyst was treated at 120 °C for 1 h. Iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), the pretreated catalyst (0.1 g) and potassium carbonate (3 mmol) were stirred for 1 h in refluxing ethanol (5 ml). Then the solid was separated by filtration, and then washed by ethanol. The solvent was evaporated. The residue was subjected three times to extraction with dichloromethane–water. Anhydrous sodium sulphate was used to eliminate the residual water from the organic phase, then it was filtered and the solvent was evaporated. The product's structure was verified by <sup>1</sup>H NMR and/or GC–MS analysis. The catalyst was recovered by washing with ethanol and drying at 120 °C for 1 h before reuse.

1,1'-Biphenyl was isolated as white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.61–7.58 (d, 4H); 7.46–7.41 (dd, 4H); 7.37–7.34 (d, 2H);. GC:  $R_t$ : 12.101 min. MS (m/z): 154 (M<sup>+</sup>), 128, 115, 102, 76. 4-Methyl-1,1'-biphenyl was isolated as white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 2.39 (s, 3H), 7.23–7.26 (m, 2H), 7.32–7.34 (t, 1H), 7.40–7.44 (t, 2H), 7.48–7.51 (d, 2H), 7.56–7.59 (d, 2H). 3-Methyl-1,1'-biphenyl was isolated as yellow liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 2.39 (s, 3H), 7.23–7.41 (m, 4H), 7.55–7.57 (d, 2H). 2-Trifluoromethyl-1,1'-biphenyl was isolated as light yellow liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.30–7.44 (m, 7H), 7.49–7.54 (t, 1H), 7.71–7.74 (d, 1H).

Hot filtration test: The aim of this test is to evidence if a homogeneous process exists side by side of the heterogeneous one. The reaction conditions and the quantity of reactants were as described above. The Cu–Pd–MgAlO-CI catalyst was filtered out after 10 min of reaction time, then the potassium carbonate (3 mmol) was re-added and the reaction was continued in this manner until 1 h of reaction

time. The reaction mixture was worked up as described above.

#### 2.3 Catalyst Characterisation

Inductively coupled plasma optical emission spectrometry (ICP–OES) analysis was carried out on Perkin-Elmer Optima 2000DV to quantify the metal content on the support.

Specific surface area of MgAlO and the impregnated supports were measured by nitrogen adsorption and desorption at -196 °C with BET (Brunauer–Emmett–Teller) surface analyser (Micromeritics Model TRISTAR 3000) using BET–BJH (Barrett–Joyner–Halenda) method after drying each material in anaerobic chamber for 12 h. X-ray powder diffraction (XRD) patterns of samples were obtained with a PANalytical, Empyrean diffractometer using CuK $\alpha$  radiation from 10° to 90° (in 2 $\theta$ ) with 0.017° steps. XRD patterns were compared with references extracted from PAN-ICSD (PANalytical version of the ICDD (International Centre for Diffraction Data)) and ICDD—PDF-2 Release 2003 to identify the crystalline phases.

Transmission electron microscopy (TEM)/energy-dispersive x-ray spectroscopy (EDS) (JEM-2100 LaB6 TEM) was used to determine the dispersion of Cu and Pd particles on the surface of MgAlO and EDS mapping was performed to visualize elemental and spatial information of Cu and Pd on the MgAlO surface.

Temperature programmed reduction (TPR) experiments were performed to investigate the distribution and reducibility of Cu and Pd particles. Each catalyst—both mono- and bimetallic—after drying at 120 °C for 5 h were introduced into a quartz glass reactor for the TPR analysis and examined in the temperature range of 30–600 °C with ramping of 5 °C/min. After purging the reactor with argon, 1 % H<sub>2</sub>/Ar pulses were introduced through the system bed at the flow rate of 30 ml/min. The H<sub>2</sub> consumption was determined by Thermal Conductivity Detector (TCD).

Basicity was measured by adsorption of carbon dioxide followed by Fourier transform infrared spectroscopy (FT-IR). To this purpose carbon dioxide was adsorbed at room



Fig. 1 The Suzuki-Miyaura coupling of phenylboronic acid with iodobenzene

Table 2 Catalyst screening for the Suzuki–Miyaura reaction

Catalyst	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	TOF $(h^{-1})^c$
No catalyst	<5	<5	n/a
MgAlO	<5	<5	n/a
Cu–Pd–MgAlO-CI	100	100	170.4
Cu–Pd–MgAlO-TSI	100	100	526.3

Reaction conditions: phenylboronic acid (1.5 mmol), iodobenzene (1 mmol), potassium carbonate (3 mmol), 0.1 g (1.8 mol% Pd and 8.5 mol% Cu) with Cu–Pd–MgAlO-CI catalyst and (1.7 mol% Pd and 8.82 mol% Cu) with Cu–Pd–MgAlO-TSI in EtOH, 78 °C, 1 h

<sup>a</sup> Isolated yield of biphenyl

<sup>b</sup> Conversion of iodobenzene

<sup>c</sup> At 1 h, calculated assuming that the number of the atoms on the surface is the amount of the catalyst active phases. Ignoring the exact repartition between Cu and Pd, the average of the two values  $D \times d$  corresponding to each metal was used

temperature (RT) by the addition of known amount of  $CO_2$  gas. Then the sample was kept under vacuum  $(10^{-6} \text{ mbar})$  at room temperature to remove the physisorbed carbon dioxide. Then FT-IR spectra were recorded from RT to 450 °C by 50 °C steps. Final spectra were generated by the subtraction of reference spectra from the measured spectra.

## **3** Results and Discussion

Wet impregnation was selected as preparation for the four catalysts studied: Cu–MgAlO, Pd–MgAlO as monometallic catalysts; Cu–Pd–MgAlO-TSI and Cu–Pd–MgAlO-CI as bimetallic catalysts. The catalysts were tested in the Suzuki–Miyaura reaction.

## 3.1 Catalytic Test in the Suzuki-Miyaura Reaction

The Cu–Pd–MgAlO catalysts were tested in the reaction of phenylboronic acid with iodobenzene in the presence of potassium carbonate as base in ethanol as solvent (Fig. 1).

In the first experiments these catalysts showed the same activity as the Pd–Cu–4A catalysts earlier, the corresponding product—biphenyl—was obtained with quantitative preparative yield in the presence of Cu–Pd–MgAlO catalysts (Table 2).

# 3.1.1 Hot Filtration Test

Hot filtration test was performed to ascertain the heterogeneous nature of the Cu–Pd–MgAlO-CI catalyst. The catalytic material was eliminated at 10 min and the reaction was continued in the absence of the catalyst with the



Fig. 2 Stability of the catalysts Cu–Pd–MgAlO in the Suzuki model reaction

afresh added  $K_2CO_3$  base. After the workup of the reaction mixture the reaction showed to be incomplete resulting biphenyl with 73 % preparative yield. No evolution of the conversion and the yield were observed whereas in the presence of catalyst, the reaction goes further to reach 100 % of conversion and a yield up to 99 %. These results are a good indication that no homogeneous process is predominant during this reaction under our working conditions. The test proved that by eliminating the catalytic material the reaction stopped completely. Thus the experimental test 'hot filtration' evidences the heterogeneous nature of the catalytic system.

## 3.1.2 Stability

The stability of the TSI and CI catalysts prepared with two methods was tested in the Suzuki model reaction between phenylboronic acid and iodobenzene. We wished to examine if there was a difference between the stability of the two materials. The results are reported in Fig. 2. The activity of the catalyst prepared with CI did not change even after six catalytic runs, while the samples prepared with TSI showed decreasing activity after the 5th cycle: the quantitative preparative yield decreased to 80 % yield. In our previous work we found that the catalyst prepared with TSI was more stable in case of 4A support due to the higher presence of Cu/Pd 1:1 particles [35], while in this study with MgAlO the method CI proved to result in a more stable catalyst for the Suzuki–Miyaura coupling. Thus depending on the nature of the support different catalyst preparation method gives a more stable catalyst. Moreover, as it was evidenced below in the characterization part, this improvement in stability is linked to the amount of Cu/Pd 1:1 particles whatever the preparation used.

#### 3.1.3 Differences in the Kinetics

To compare the kinetics of the catalysts supported on MgAlO and 4A the model reaction was carried out with the two most stable catalysts, namely with Cu–Pd–4A-TSI and Cu–Pd–MgAlO-CI. To study the differences in the rate of the reaction 10, 30 and 60 min experiments were carried out. The results obtained are shown in Table 3. It is interesting to observe that while with the catalyst supported on 4A 60 min were required for the completion of the reaction time, 30 min were sufficient. This difference in the reaction rate is a crucial point in catalyst selection in an economic point of view.

### 3.1.4 Effect of the Quantity of the Base

The impact of the reduction of base's quantity was also studied. We wanted to find out if a support with stronger basic properties can possibly lead to the elimination of the

Entry Reaction time		Cu–Pd–4A-TSI			Cu–Pd–MgAlO-CI				
(min)	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	$TOF (h^{-1})^{c}$	Particle size (nm)	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	$TOF (h^{-1})^{c}$	Particle size (nm)	
1	10	63	88	14.7	2.5	73	90	124.4	15.6
2	30	73	94	17.0		>99	100	170.4	(heterogeneous)
3	60	>99	100	23.3		>99	100	170.4	

Table 3 Kinetics of the Suzuki-Miyaura reaction with Cu-Pd-4A-TSI and Cu-Pd-MgAlO-CI

Reaction conditions: phenylboronic acid (1.5 mmol), iodobenzene (1 mmol), potassium carbonate (3 mmol), 0.1 g catalyst (2 mol% Pd and 9 mol% Cu) with Cu–Pd–4A-TSI and (1.8 mol% Pd and 8.5 mol% Cu) with Cu–Pd–MgAlO-CI in EtOH, 78 °C

<sup>a</sup> Isolated yield of biphenyl

<sup>b</sup> Conversion of iodobenzene

<sup>c</sup> At 1 h, calculated assuming that the number of the atoms on the surface is the amount of the catalyst active phases. Ignoring the exact repartition between Cu and Pd, the average of the two values  $D \times d$  corresponding to each metal was used

Table 4 Effect of the base reduction on the Suzuki-Miyaura reaction yield in the presence of Cu-Pd-4A-TSI and Cu-Pd-MgAlO-CI

Quantity of base (eq)	Cu–Pd–4A-TSI			Cu–Pd–MgAlO-CI		
	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	TOF $(h^{-1})^c$	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	TOF $(h^{-1})^c$
3	>99	100	23.3	>99	100	170.4
2.5	80	100 <sup>e</sup>	18.6	>99	100	170.4
2	80	100 <sup>d</sup>	18.6	87	100 <sup>d</sup>	148.2
1.5	80	100 <sup>d</sup>	18.6	80	100 <sup>d</sup>	136.3
1	80	100 <sup>d</sup>	18.6	80	100 <sup>d</sup>	136.3

Reaction conditions: phenylboronic acid (1.5 mmol), iodobenzene (1 mmol), potassium carbonate (3 mmol), 0.1 g catalyst (2 mol % Pd and 9 mol % Cu) with Cu–Pd–4A-TSI and (1.8 mol % Pd and 8.5 mol % Cu) with Cu–Pd–MgAlO-CI in EtOH, 78 °C, 1 h

<sup>a</sup> Isolated yield of biphenyl

<sup>b</sup> Conversion of iodobenzene

 $^{c}$  At 1 h, calculated assuming that the number of the atoms on the surface is the amount of the catalyst active phases. Ignoring the exact repartition between Cu and Pd, the average of the two values D x d corresponding to each metal was used

<sup>d</sup> Byproduct: 2,4,6-triphenyl-cycloboroxane

**Table 5**Scope of the Cu–Pd–MgAlO-CI catalyst in theSuzuki–Miyaura coupling

Boronic acid	Aryl halide	Yield (%) <sup>a</sup>	Conversion (%) <sup>b</sup>	TOF $(h^{-1})^c$
ОН В ОН	Br	>99	100	170.4
ОН В ОН	Br	80	91	136.3
ОН В ОН	GF3	86	100	146.5
он В он	Br	>99	100	170.4
ОН В ОН	СІСНО	_d	-	n/a

Reaction conditions: phenylboronic acid (1.2 mmol), aryl halide (1 mmol), potassium carbonate (3 mmol), 0.1 g catalyst (1.8 mol % Pd and 8.5 mol % Cu) Cu–Pd–MgAlO-CI in EtOH, 78 °C, 1 h

<sup>a</sup> Isolated yield of biphenyl derivative

<sup>b</sup> Conversion of aryl halide

 $^{c}$  At 1 h, calculated assuming that the number of the atoms on the surface is the amount of the catalyst active phases. Ignoring the exact repartition between Cu and Pd, the average of the two values D x d corresponding to each metal was used

<sup>d</sup> Reaction time: 2 h 15 min

base as much as we wanted to determine the role of the base. Is it only needed in the catalytic cycle or it has also a role to stabilise the catalyst to restore the support's basicity? To answer this question the model reaction (Fig. 1) was carried out with Cu–Pd–4A-TSI catalyst and Cu–Pd– MgAlO-CI. These catalysts previously proved to be stable and active even after six cycles. Table 4 shows the results obtained. Originally in the reaction three equivalents of base were applied. In case of 4A by decreasing the quantity of the base even with a half equivalent (i.e. 2.5 equivalents of  $K_2CO_3$  were used), the yield of biphenyl dropped significantly while in case of MgAlO support, the same reduction still leads to quantitative yield (the biphenyl production is >99 %). In the presence of 1.5 eq base and MgAlO support, the same result was obtained as with 2.5 eq base and 4A support,

Table 6     Metal content and
BET surface area of the mono
and bimetallic catalysts on
$(MgO)_{0.75}(Al_2O_3)_{0.25}$ support

Catalyst	Targeted val	ues	Measured values (ICP)		BET surface
	Cu (wt%)	Pd (wt%)	Cu (wt%)	Pd (wt%)	area (m²/g)
MgAlO	-	_	-	_	165
Cu–MgAlO	6.3	_	5.9	_	115
Pd–MgAlO	_	2.1	_	1.9	150
Cu-Pd-MgAlO-TSI	6.3	2.1	5.6	1.8	140
Cu–Pd–MgAlO-CI	6.3	2.1	5.4	1.9	120

namely 80 % yield. Our results thus show that even though the stronger basic character of the support does not allow us to eliminate the inorganic base from the reaction mixture, our Cu–Pd–MgAIO-CI catalyst can work with a slightly reduced quantity of base. However in case of 4A support, at least three equivalents of base are needed to perform the reaction and to stabilize the catalyst.

#### 3.1.5 Scope of the Reaction

The scope of the reaction was studied to ascertain that heterogeneous coupling takes place and also to examine the less activated coupling agents for the Suzuki–Miyaura coupling such as bromobenzenes and chlorobenzene substituted in different positions. The results obtained are summarized in Table 5.

One can conclude that during 1 h reaction time the bromobenzene derivatives undergone the coupling resulting the heterocoupled product from good to excellent yield regardless the position of the subtituent (o-, m-, p-position either on the bromobenzene or on the boronic acid). The chloro derivative proved to be unreactive.

These observations together urged us to continue our experiments by focusing on the characteristics of the catalysts in order to study the effect of the nature of the support on the properties of a catalyst to explain the differences between the performances of catalysts supported on MgAIO and 4A. The catalysts were characterized by ICP, BET, XRD, TEM, EDS, TPR and FT-IR.

#### 3.2 Catalysts Characterisation

ICP–OES analysis was performed to determine the real metal content and evidenced that the results were in accordance with the expected values. A slightly lower metal content was obtained than the targeted one but all the samples can be compared with each other (Table 6). These values were lower as those of 4A supported catalysts (Table 1).

Measurements of the surface area using BET method evidenced that the support MgAlO changed from 165 to 140 m<sup>2</sup>/g in the first case (TSI) and to 120 m<sup>2</sup>/g in the second case (CI) (Table 5). Similar data were obtained

earlier for the Cu–Pd–4A catalysts [35]. This can be explained by the difference in the preparation method. TSI is a two-step process whilst CI takes place in one step. The preparation in several steps allows the sintering of the particles during thermal treatments leading to more free sites and thus higher surface area. The pore volume of the mixed oxides increased from 0.348 to 0.396 cm<sup>3</sup>/g in case of TSI and to 0.370 cm<sup>3</sup>/g when the catalyst was prepared with CI. The average pore size in case of TSI was 112 and 122 Å for CI. Adsorption isotherms of the supports and catalysts for gas–solid equilibria belong to Type IV of IUPAC classification indicating that the materials are mesoporous ones.

According to XRD analysis, the crystallised phases of the support consisted—for the most part—of periclase (98-000-9863, Mg<sub>1</sub>O<sub>1</sub>, cubic) and of aluminium oxide-gamma (98-003-0267, Al<sub>2.666</sub>O<sub>3.999</sub>, cubic) (Fig. 3a). Thus, the two oxides MgO and Al<sub>2</sub>O<sub>3</sub> co-exist to form the support. In addition to these signals in the bimetallic catalysts' diffractograms signs of metallic particles were also identified. To demonstrate it the 20 values between 30° and 80° are represented in Fig. 3b. In both TSI and CI cases mostly copper–palladium oxide (00-044-0185, CuPdO<sub>2</sub>, tetragonal) and palladium (98-006-4920, Pd<sub>1</sub>, cubic) in minority were found. These particles differ from those found on the surface of the 4A supported catalysts. Here the signs of the metallic parts were significant compared to those of the supports suggesting a bigger particle size.

The morphology of the support was found to be highly crystallised by the TEM analysis. Concerning the metallic particles, heterogeneous particle size was observed on the surface of the TSI catalyst (Fig. 4a, b).

The small particles were between 1 and 10 nm with a 4.9 nm average particle size for Cu–Pd–MgAIO-TSI (Fig. 5). Few big particles up to hundreds of nanometres can be seen, but most of them are under 100 nm. The overall average particle size was 49 nm but as it can be seen in Fig. 5, for TSI catalyst, the majority of the particles consists of particles between 1 and 10 nm. As for the particles composition, EDS analysis allowed us to see that the metallic particles consisted of Cu/Pd with an atomic ratio 1:1. On the surface of MgO-Al<sub>2</sub>O<sub>3</sub> besides the copper–palladium crystals, copper-rich parts were also

**Fig. 3** XRD diffractograms **a** of the support and fresh TSI and CI catalysts, **b** zoom into determine metal crystals (*lozenge*) Cu–Pd–MgAIO-TSI; (*dagger*) Cu–Pd–MgAIO-CI; (*section sign*) palladium 98-006-4920; (*ampersand*) CuPdO<sub>2</sub> 00-044-0185; (*number sign*) periclase 98-000-9863; (*currency sign*) γ-Al<sub>2</sub>O<sub>3</sub> 98-003-0267



observed, mostly at the areas of smaller particle size (Fig. 4a, b). On the catalyst prepared by CI procedure the metallic particles were also present at heterogeneous size (Fig. 4c, d). Their size were between 0.7 and 4.4 nm with a 1.9 nm average particle size, which is a narrower size distribution than in case of TSI (Fig. 5). However the overall distribution is larger and an important amount of particles between 10 and 50 nm can be pointed out on CI whereas on TSI a bimodal distribution can be seen with small particles and very big particles. Thus, the average size of particles is higher on TSI than on CI (49 vs 15.6 nm). The EDS analysis showed that Cu/Pd 1:1 and Cu/Pd 2:1 were present. Copper particles were also dispersed on the support which is again highly crystallised. The heterogeneity of the particle size and the average particle size is a considerable difference between MgAlO and 4A supported Cu-Pd catalysts.

Reducibility of Pd–Cu particles on MgAlO support was examined by H<sub>2</sub>-TPR measurement. The results obtained

are shown in Fig. 6 as hydrogen uptake in the function of heating temperature for the monometallic catalysts and for the bimetallic catalysts as well.

It should be noted that all catalysts were calcined at 600 °C during the preparation so that the metals in oxide forms were obtained. The TPR profile of Pd-MgAlO showed two peaks, the first one at 30-120 °C (maximum at 75 °C) and the second one at 125–370 °C (maximum at 200 °C). The first peak is corresponding to the reduction of PdO crystallites to Pd<sup>0</sup> metal [42]. This reduction takes place in one step. In our case a second peak was also present at 200 °C, which can be attributed to the reduction of Pd species strongly interacting with the support. Magnesia is a reportedly interacting support [45, 46]. Pd is also able to form Pd-hydride which is generated by the absorption of hydrogen into the sub-surfaces of the metallic Pd [47, 48]. In a TPR profile it is represented by a negative peak corresponding to its decomposition. In our case the formation of these species was not observed. This can be

Fig. 4 TEM images of fresh catalysts: **a**, **b** images of Cu–Pd–MgAlO-TSI; **c**, **d** images of Cu–Pd–MgAlO-CI



attributed to the relatively small palladium particles as it is reported that the smaller the Pd particle size the lower the solubility of the hydrogen is [49]. The quantitative analysis of the peaks showed that the measured hydrogen uptake is in a large excess compared to the theoretical hydrogen consumption (Table 7, entry 1). This indicates the disappearance of palladium-hydrides without negative peaks. It is important to note that as palladium absorbs hydrogen the reduction state of the palladium cannot be determined based on the ratio between measured and theoretical hydrogen consumption. During the reduction of Cu-MgAlO sample a single peak was observed, starting at 145 °C with a maximum at 250 °C. The area under the peak corresponds well with the theoretical hydrogen consumption for the complete reduction of CuO to Cu<sup>0</sup>. The temperature of the reduction and also the quantitative analysis (Table 7, entry 2) substantiates this statement [50]. During the temperature programmed reduction of the bimetallic catalysts' different profiles were observed. In both cases two peaks were detected. Concerning Cu-Pd-MgAlO-TSI a peak at 66-123 °C was present, which might be attributed to the reduction of PdO, while the peak at 160-343 °C consist of the reduction of two different species: First the reduction of palladium species (as seen the reduction peak at Pd-MgAlO at 200 °C) takes place, which have different particle size as the species reduced around 100 °C. After the reduction of palladium particles the reduction of Cu/Pd alloy happens. As their temperatures are close to each other we see this process as one H<sub>2</sub> consumption peak with a head at 240 °C. This temperature is slightly lower than the maximum at Cu-MgAlO (250 °C). It is reported in the literature for Cu-Pd catalysts [51] that by the addition of the palladium, the reduction temperature seen at the monometallic copper catalyst decreases. It can be attributed to the hydrogen spillover from palladium to copper, which facilitates the reduction and suggest the proximity of the two metals. As for the ratio between theoretical and actual hydrogen consumption it gave 0.60 (Table 7, entry 3). For Cu-Pd-MgAlO-CI the first peak contributed to palladium reduction is also present at 56-127 °C while the second peak has a different shape at 153-347 °C as it had in case of TSI and a lower maximum at 220 °C. We assume that in case of CI first it consists of the reduction of Cu/Pd alloy which is followed by the reduction of copper particles, as in this case the peak has a tail. The lower maximum of this peak suggests that the hydrogen spillover from the palladium is even more important in the case of this catalyst. The ratio between the



Fig. 5 Particle size distribution of Cu-Pd-MgAlO-TSI and Cu-Pd-MgAlO-CI



Fig. 6 TPR profiles of mono-and bimetallic catalysts

calculated and measured  $H_2$  consumption in this case was 0.76 (Table 7, entry 4). These results are consistent with the DRX, TEM and EDS data.

The basic properties of the two supports (4A, MgAlO) and the two most stable Cu–Pd catalysts (Cu–Pd–4A-TSI, Cu–Pd–MgAlO-CI) were studied by the adsorption of

carbon dioxide followed by FT-IR. Our aim was to ascertain the differences in basicity and to study how the impregnation affects the basic characteristics of the supports. All spectra are subtracted spectra taken from RT to 450 °C by 50 °C steps. The spectrum of the support MgAlO is complex, containing several vibrations. The vibration of bicarbonates formed from basic hydroxyls and carbon dioxide is situated at 1234 cm<sup>-1</sup> ( $\delta_{C-OH}$ ). The pairs of signs at 1310/1697 cm<sup>-1</sup> can be associated with the vC=O vibrations and at  $1382/1600 \text{ cm}^{-1}$  with v(OCO)s and v(OCO)a of bidentate carbonates. [52] 1427 cm<sup>-1</sup> is attributed to the v(OCO)s. The bands at 1475 and 1648  $\text{cm}^{-1}$  correspond to (vC=O)a and the band at 1520 cm<sup>-1</sup> can be assigned to the v(OCO)a of monodentate carbonate. Higher bands were also present at 2854, 2915 and 3545  $\text{cm}^{-1}$ , the latest corresponding to vOH. On Cu-Pd-MgAlO-CI sample less signals appeared compared to the support alone. The band corresponding to  $\delta_{C-OH}$ vibration (at 1234 cm<sup>-1</sup>) disappeared after impregnation of the support, the bands shifted and their shape became more regular in case of bimetallic catalyst. Bands were observed at  $1363/1630 \text{ cm}^{-1}$  assigned to vC=O vibrations of two different bidentate carbonate structures, and the band at  $3542 \text{ cm}^{-1}$  corresponding to vOH. The spectrum of 4A

**Table 7** Quantitative TPRanalysis for bimetallic andmonometallic catalysts

Entry	Catalyst	$H_2$ consumption/g catalyst (mmol/g) <sup>a</sup>	Ratio <sup>b</sup>
1	Pd-MgAlO	1.58	8.72
2	Cu–MgAlO	0.90	0.97
3	Cu-Pd-MgAlO-TSI	0.73	0.60
4	Cu-Pd-MgAlO-CI	0.69	0.76

<sup>a</sup> Total measured H<sub>2</sub> consumption/mass of the sample

 $^{\rm b}$  Total measured  $\rm H_2$  consumption/total theoretical  $\rm H_2$  consumption assuming the presence of CuO and/or PdO species



Fig. 7 Subtracted spectra after evacuation at room temperature of 20 mg material

consisted of a band at 2300 cm<sup>-1</sup> corresponding to the v(OCO)a of physisorbed CO<sub>2</sub> [53]. The bands observed in the region of  $1200-1700 \text{ cm}^{-1}$  can be associated with chemisorbed CO<sub>2</sub> species. These include either CO<sub>2</sub> molecules adsorbed on the cations in a linear configuration  $(v_2 \text{ band})$  or in form of carbonate/bicarbonate ions. [54] The sign at  $3461 \text{ cm}^{-1}$  corresponding to vOH was also observed. On the Cu-Pd-4A-TSI sample the signals differed from those of the support alone. The band at 2350  $\text{cm}^{-1}$  corresponding to the v(OCO)a of physisorbed CO2 was present on the RT and 50 °C sample as well, but by increasing temperature the band disappeared. All bands disappeared completely above 150 °C. The band at  $1660 \text{ cm}^{-1}$  corresponded to the (vC=O)a of hydrogencarbonate species formed after the interaction between CO<sub>2</sub> and surface hydroxyl groups.

It can be evidenced from the FT-IR measurements that the basicity of the supports changed during the catalyst preparation. In the literature no coefficient related to the capacity of a material for the adsorption of carbon dioxide exists. To obtain quantitative information on the basicity among these four materials the area of the bands between 1670 and  $1310 \text{ cm}^{-1}$  were taken into account. These bands correspond to bidentate carbonates generally related to basicity. The spectra after evacuation under vacuum at room temperature were used to compare the materials (Fig. 7).

Table 8 shows the quantitative values in order to compare the catalysts. The area per support decreases from MgAlO to Cu–Pd–MgAlO-CI indicating that after the preparation of the bimetallic catalysts several surface hydroxyl groups and basic oxygen are covered, and/or no longer available for carbon dioxide molecules adsorption. The density of basic hydroxyl groups showed that MgAlO and Cu–Pd–MgAlO-CI exhibit significantly stronger basic properties than 4A or Cu–Pd–4A-TSI. We can conclude from the FT-IR study that according to the values of the bands area expressed by m<sup>2</sup> of support, the ranking of the materials is MgAlO > Cu–Pd–MgAlO-CI > 4A > Cu– Pd–4A-TSI.

#### 3.3 Discussion

In our paper the effect of the support and effect of the quantity of the base in the Cu-Pd catalysed Suzuki-Miyaura reaction were examined. The catalysts were prepared with wet impregnation on (MgO)<sub>0.75</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.25</sub> support. This support was selected taking into account the results of a previous study [41] showing that it possesses high basicity along with relatively high surface compared to other MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxides with different ratios. Two preparations were used to obtain samples (two-step impregnation and coimpregnation). The catalytic tests were performed in the Suzuki-Miyaura cross coupling reaction where the activity and stability of the catalysts were examined. It was found that the catalyst prepared with CI was more stable if the support was MgAlO. During our previous study [35] we found that in case of Cu-Pd supported on 4A the TSI catalyst was more stable in this reaction. Although depending on the nature of the support a different preparation method proved to result an active and stable catalyst, these results are in accordance as these preparation methods accelerate the formation of the active phase Cu/Pd 1:1 alloy with small (2.5 nm) and relatively small (15.6 nm) particle size. We can conclude that whatever the preparation method is, the aim is the formation of Cu/Pd 1:1 particles with small particle size.

Taking an insight to the kinetics of the reaction by the catalysts supported on 4A and MgAlO it was evidenced

**Table 8** Area of the bands located between 1310 and 1670  $\text{cm}^{-1}$  for the supports and bimetallic catalysts

Material	Area (a.u.)	Area of bands expressed per g of support (a.u./g)	Area of bands expressed per m <sup>2</sup> of support (a.u./m <sup>2</sup> )
MgAlO	20.5	1072	6.50
4A	30.8	758	0.95
Cu–Pd–MgAlO-CI	8.9	377	3.14
Cu-Pd-4A-TSI	1.1	29.5	0.10

that the reaction takes place in 30 min by the Cu-Pd-MgAlO-CI catalyst, while with Cu-Pd-4A-TSI it requires the double of this reaction time, 1 h. It is an important finding as MgAlO has a drawback compared to 4A, as 4A is a readily available support, while MgAlO needs to be prepared. Taking in account that the reaction rate is faster with Cu-Pd-MgAlO-CI, the catalytic process is more economic, the application of Cu-Pd supported on MgAlO is favoured compared to that of Cu-Pd on 4A. Based on the characteristics of the catalysts and the experimental results one can conclude that the composition of the bimetallic particles (Cu/Pd 1/1) is more important than the particle size, as catalysts with particles of different size gave comparable conversions. In addition it is the kinetics that has impact on the yield and TOF, which is influenced by the basicity of the support. We can conclude that the support has an effect on the catalytic performances but not the particle size, as comparable results were obtained over the catalysts with the same support.

According to the elimination/reduction of the quantity of the base, first the function of the base in this catalytic cycle should be studied and described. The role of the anionic bases and their charge-balancing cations were thoroughly studied by Amatore et al. [55–57] in the catalytic cycle of the palladium catalysed Suzuki-Miyaura reaction where inorganic base was used. It was found that inorganic bases do not play the role of base but they serve as a ligand for aryl-palladium(II) complexes. They play four kinetically antagonistic roles. These anionic bases take part in the formation of the reactive species in the rate-determining transmetallation step and they catalyse the reductive elimination of the corresponding intermediate, which are both positive roles. As negative function they form unreactive aryl boronates and they can be complexated by the charge-balancing cation before the transmetallation step.

These previous studies allow us certain conclusions. Our experiments to study the effect of the quantity of the base on the Cu–Pd catalysed Suzuki–Miyaura reaction were carried out with the two catalysts most stable: Cu–Pd–4A-TSI and Cu–Pd–MgAlO-CI. As the quantity of the  $K_2CO_3$  was diminished with 4A the yield dropped significantly. Already

0.5 equivalent less base (with 2.5 eq  $K_2CO_3$ ) results in 80 % yield instead of quantitative. On the other hand the decrease of the yield is more gradual with MgAlO. As the MgAlO is not just present as a recoverable base but as a support it only allows us to slightly decrease the quantity of base applied while keeping its activity and role as a support.

As for the TOF obtained with the Cu-Pd-MgAlO catalysts the values were between 136 and 170  $h^{-1}$ , which is very much comparable with the TOF of other heterogeneous systems. The coupling of aryl bromides with phenylboronic acids took place with 16–198  $h^{-1}$  TOFs in DMF/water over zeolite confined Pd nanoclusters [58], Pdmontmorillonite catalysed the Suzuki coupling with TOFs  $60-356 \text{ h}^{-1}$  [59]. Comparing the results with homogeneous catalytic systems conclusions are hard to draw as TOF depends highly on the nature of the ligands, the metal loading and the solvents. For example with a palladiumdipyridylmethylamine complex depending on the metal loading (0.00076-1 mol% Pd) and reaction media (DMF/ H<sub>2</sub>O, H<sub>2</sub>O, MeOH/H<sub>2</sub>O) the obtained TOFs varied between 2 and  $10^5 \text{ h}^{-1}$  [60]. In a further paper depending on the ratio between Pd(dba)<sub>2</sub> and R-Phos, a phosphine-arene ligand, TOFs between 80 and 1662 h<sup>-1</sup> were obtained in the reaction of aryl chlorides with arylboronic acid in dioxane at 100 °C [61].

# 4 Conclusion

Overall an air-stable Cu-Pd bimetallic catalyst supported on MgAlO was developed for the ligand free Suzuki-Miyaura reaction. The catalyst was prepared by TSI and CI. Their catalytic behaviour differed in the stability whereas the catalyst prepared with CI, containing Cu/Pd 1:1 alloy with smaller particle size proved to be stable for six runs contrary to TSI. A crucial difference between the MgAlO and 4A supported catalyst in the Suzuki-Miyaura reaction is that by MgAlO supported Cu-Pd bimetallic catalyst; the reaction time can be reduced to 30 min to the complete conversion of iodobenzene to biphenyl. Moreover we concluded that with a more basic support the reduction of the quantity of the base is possible to a certain extent without decreasing activity. The catalyst characterization methods showed that the most significant differences were in the particle size between the Cu-Pd catalysts supported on MgAlO and 4A.

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