



## Short communication

## Solid sheet of anodic aluminium oxide supported palladium catalyst for Suzuki coupling reactions



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## ABSTRACT

A Pd(II) Schiff base complex supported on anodic aluminium oxide (with Al substrate sheet) was successfully prepared. The prepared nanocatalyst was characterized by SEM, TEM and XPS. The synthesized Pd-based catalyst showed excellent catalytic activity for Suzuki cross-coupling reactions under mild conditions. The catalytic activity did not deteriorate after five repeated cycles. Pd(II) Schiff base complex supported on solid sheets could be separated and recovered easily by taking it out of the reaction solution. The construction of solid sheet supported Pd catalyst would be expected to be a promising system to perform heterogeneous catalytic reactions.

## 1. Introduction

Palladium catalyzed carbon-carbon bond-forming reactions have played a crucial role in synthetic organic chemistry, which have been widely applied to diverse areas such as natural products, functional polymer materials and pharmaceuticals. The Suzuki coupling reaction is one of the most widely used methods for the carbon-carbon bond-forming reactions. Traditionally, many palladium catalysts used in such reactions are homogeneous, such as  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $[\text{Pd}(\text{OAc})_2]$  and  $[\text{PdCl}_2(\text{PPh}_3)_2]$  [1–5]. Although these catalysts present excellent activity, there remain problems that need to be addressed. On the one side, most of the ligands are of high cost, sensitive to air oxidation and thus require air-free conditions, which pose significant inconvenience for applications [6,7]. On the other side, the product of extraction is time-consuming and impossible to be recovered in consecutive reactions. As a potential solution, immobilization of Pd nanoparticles on solid support, such as polymers [8,9], zeolites [10], silica spheres [11,12], magnetic particles [13,14] and carbon nanotubes [15–20] have recently received considerable attention as a new generation of heterogeneous catalysts. However, supported Pd catalysts have some disadvantages. For example, a loss of catalyst could occur after recovered by filtration [21]. Also, leaching and aggregation of Pd nanoparticles from the support might occur. For example, Pd nanomaterials supported on functionalized silica were slowly deactivated after three runs in Suzuki coupling reactions [22]. Recently, M. Gómez and co-workers [23–25] presented a new system of palladium nanoparticles immobilized in a glycerol phase. The innovative dual homogeneous/heterogeneous catalytic colloidal solution had been proved by its efficient application in carbon-carbon bond-forming reactions and could be

recycled more than ten times with high activity. In all, the development of Pd catalysts offering high activity, stability and easy separation is the focus subject.

Nanometer-sized supports have recently attracted a great deal of interest because of their high surface area and outstanding stability and activity [26]. Anodized aluminium oxide (AAO) containing ordered cylindrical tunable nanochannels with 10 nm–500 nm has been maturely developed in the past two decades. These channels have been used as template for the preparation of a wide range of nanomaterials in the forms of nanodots, nanowires, nanotubes, etc. [27–29]. Usually, AAO was prepared by electro-oxidation on an aluminium sheet in inorganic acids [30,31]. The aluminium substrate and the compact barrier layer (intercalated layer) were then removed with acids or bases to obtain through-hole AAO membranes [32]. Then nanomaterials were fabricated using the through-hole AAO. This process is time-consuming and causes also environmental contamination. An important shortcoming of this method, however, is that the through-hole AAO's are very brittle, thin, and difficult to handle during nanomaterial fabrication. Non-through-hole AAO (containing Al substrate, marked AAO@Al) is a solid sheet and can be cut into different sizes. Considering the solid sheet as support, the heterogeneous catalysts can be easily separated and recovered just by taking them out of the solution. Combining the ordered porous structure and the advantage of nanometer-sized solid sheet supports, nanomaterials supported on AAO@Al is a potential research subject. Recently Li et al. [33] have synthesized successfully Pd nanowires confined on AAO@Al. The catalysts showed great activity, stability and reusability in Suzuki carbon-carbon coupling reactions. They reported that the nanoarrays are confined in the pores of AAO and were not easily agglomerated. To the best of our

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knowledge, AAO@Al supported metal catalysts have been rarely reported. Here, we prepared a novel Pd(II)-AAO@Al catalyst through the incorporation of schiff bases. The application of the solid sheets supported Pd-based catalyst as a heterogeneous catalyst in Suzuki reactions is reported herein. The results showed that Pd(II) complex anchored on the functionalized AAO presents great activity, stability and reusability, which demonstrates a promising strategic approach in the field of heterogeneous nanocatalysis.

## 2. Experimental

### 2.1. Materials and physical measurements

Palladium chloride, ethylene glycol, oxalic acid, phosphoric acid, chromium trioxide, acetone and ethanol were purchased from Guangzhou Chemical Reagent Factory in the highest available purity and used without further purification. The high purity Aluminium sheets (99.99%) were purchased from NanChang Mat-Cn. The morphologies of the nanomaterials were examined by scanning electron microscopy (SEM, Zeiss ULTRA 55). Transmission electron microscopy (TEM) studies were conducted using a PHILIPS TECNAI 10 equipment in conjunction with energy dispersive x-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) analysis was conducted using a ESCALAB 250 (Thermo Scientific, USA). The binding energy was calibrated with respect to C (1 s) at 284.6 eV. Peak deconvolution and fitting procedures were performed using XPSPEAK Version 4.1 software. The Pd content of catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a 5300DV (PE, USA).

The yield of Suzuki reaction was analyzed via gas chromatography. The measurements were performed on an Agilent GC-6820 chromatograph with a 30 m (column height)  $\times$  0.32 mm (column diameter)  $\times$  0.5 mm (column coating thickness) OV-17 capillary column with a flame ionization detector.

### 2.2. Preparation of AAO@Al

The AAO used in this work was prepared according to the procedure previously reported [33]. Briefly, the high purity Aluminium sheet (0.5 mm thickness) was annealed at 500 °C for 4 h and rinsed thoroughly by acetone and ethanol. Then, the sheet was electrochemically polished by a mixture of ethanol and perchloric acid (volume ratio of 4:1). After that, the sheet was first anodized in 0.3 M oxalic acid solution at 0 °C and 40 V for 2 h. The formed alumina film was then removed in a mixture of 6 wt% H<sub>3</sub>PO<sub>4</sub> and 1.8 wt% H<sub>2</sub>CrO<sub>4</sub> at 60 °C for 2 h, while the second anodization was conducted under the same conditions as the first anodization but for 8 h. The synthesized AAO membrane formed on the surface of Aluminium sheet was labeled as AAO@Al.

### 2.3. Preparation of AAO@Al – supported Pd catalyst

Pd-Schiff base complex supported on the AAO@Al carrier was synthesized as follows. Firstly, AAO@Al was modified by putting a piece of AAO@Al (1  $\times$  2 cm) into a solution of 3-aminopropyltriethoxysilane (1 mL), glacial acetic acid (0.5 mL) and 20 mL absolute ethanol. The reaction mixtures were refluxed for 3 h in nitrogen atmosphere. The sheet was taken out of solution, washed with ethanol and dried in vacuum. Then, the modified AAO@Al sheet was added into a solution of 3,5-di-tert-butyl-salicylaldehyde (1:5 mol ratio to 3-aminopropyltriethoxysilane) and 20 mL ethanol followed by refluxing at 70 °C for 5 h. Lastly, a round bottomed flask was charged with a certain amount of palladium chloride and 20 mL *N,N*-dimethylformamide and modified AAO@Al sheet above and refluxed at 80 °C for 1 h. The sheet was then washed with ethanol, dried in vacuum for use and labeled as Pd(II)/AAO@Al.

### 2.4. General procedure for the Suzuki cross-coupling reactions

In a typical Suzuki cross-coupling reaction, a piece of Pd(II)/AAO@Al sheet was immersed into a mixture solution, which included 1 mmol aryl halides, 1.2 mmol arylboronic acid, 1.5 mmol NaHCO<sub>3</sub> and 5 mL solvent. The reaction was conducted at different temperatures for different times. After completion of reaction, the Al sheet was taken out and the residual was extracted with ethyl acetate. The organic layer was dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated to get the desired product. The conversions and yields were analyzed by gas chromatography, based on the peak area normalization method. For the recycling test, after completing the Suzuki reaction, the solid sheet was recovered just by taking it out of solution, washed and dried, and then reused for the next run.

## 3. Results and discussion

### 3.1. Synthesis and characterization of Pd(II)/AAO@Al

Pd-schiff base complex supported on AAO@Al was synthesized by the functionalization method. AAO@Al substrate with hydroxyl groups was aminated by (3-aminopropyl) triethoxysilane in ethanol. Then, amino-AAO@Al was functionalized with 3,5-di-tert-butyl salicylaldehyde to produce schiff base groups. Lastly, Pd(II) ions were coordinated with schiff base anchored on the surface of AAO@Al. The schematic diagram is shown in Scheme 1.

SEM and TEM measurements were carried out to observe the morphology and distribution of the samples. Fig. 1a and b show the SEM images of AAO@Al and Pd(II)/AAO@Al. The average pores size of AAO is 50 nm with rather uniform pores (Fig. 1a). After the Pd was deposited on the AAO, the morphology of AAO was slightly different (Fig. 1b). It can be seen that the original structure had not been destroyed after pure AAO was treated with functionalization and metal deposition. Compared with Fig. 1a and b, the existence of some materials on the channels of AAO is clearly distinguishable. To further research the materials, after dissolving the AAO and Al, the Pd complex was characterized by TEM (Fig. 1c). The insert figure (Fig. 1c) is the EDX analysis, which identify the presence of palladium element, whereas the existence of Fe element may be due to the impurity of aluminium sheet. It is obvious that the distribution of Pd complex was abundant and some of nanoparticles aggregated to form some clusters (Fig. 1c). After the Suzuki reaction, the Pd(II)/AAO@Al catalyst was characterized by SEM (Fig. 1d). It can be seen that the surface of Pd(II)/AAO@Al was destroyed and flower-like micrometer materials appeared. The reason is due to the fact that AAO was eroded under the basic catalytic conditions of the Suzuki reaction, which was identified by placing pure AAO@Al sheet in the 1.5 mmol NaHCO<sub>3</sub> ethanol/water solution at 60 °C for 2 h. After reaction, SEM images of AAO@Al (Fig. S1) revealed that the surface of AAO@Al was also eroded, result little similar to that shown in Fig. 1d.

XPS survey spectrum of Pd(II)/AAO@Al catalyst is shown in Fig. S2. The signals of Al2p, C1s, O1s, Pd3d were detected, confirming the presence of Pd in the complex materials. Except the above elements, the N1s and Si2p signals were also detected, which arose from 3-aminopropyltriethoxysilane during synthesis. The spectrum of Pd 3d core level is shown in Fig. S3 which was fitted into a main doublet peaks by constraining the spin-orbit separation of 5.2 eV and the ratio of doublet intensities at 3:2. The binding energy at 337.3 and 342.5 eV is attributed to Pd3d<sub>5/2</sub> and Pd3d<sub>3/2</sub>, respectively, which is in accordance with those reported for Pd(II) state [34]. Thus, XPS analysis reveals that almost all Pd element in the catalyst exists as a Pd(II) complex.

### 3.2. Catalytic performance for Suzuki reaction

The Suzuki cross-coupling reaction of 4-bromobenzaldehyde with phenylboronic acid was chosen as a model reaction to find out the

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