



Palladium supported hybrid cellulose–aluminum oxide composite for Suzuki–Miyaura cross coupling reaction

Arjun Kumbhar, Sanjay Jadhav, Santosh Kamble, Gajanan Rashinkar, Rajashri Salunkhe*

Department of Chemistry, Shivaji University, Kolhapur, 416004 MS, India

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ABSTRACT

A cellulose–aluminum oxide composite was prepared and modified with organo-functional groups by reacting with the coupling reagent $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ through Al–O–Si bonds. The amino groups confined in the composite were found to be efficient for palladium entrapment, leading to a highly active and reusable heterogeneous catalyst ($\text{Pd}@\text{Al}_2\text{O}_3\text{-CELL}$) for Suzuki–Miyaura cross coupling reaction in water and $\text{H}_2\text{O}/\text{DMF}$ (8:2) mixture at 80 °C.

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Nowadays, an important part of synthetic chemistry is based on the use of precious transition metal catalysis,¹ mainly palladium which is widely used expensive metal with a high demand. Palladium plays a versatile role in organic synthesis, especially in a variety of reactions, such as Mizoroki–Heck, Suzuki–Miyaura, Stille, Sonogashira, and Buchwald–Hartwig couplings.² Among these Suzuki–Miyaura reaction is one of the most effective for the construction of biaryl units, which are molecular components in pharmaceuticals.³ They are also present in many herbicides, alkaloids like ancistrocladine as well as in engineering materials such as conducting polymers, molecular wires, and liquid crystals.⁴

Since, palladium complexes are highly expensive and sometimes responsible to contamination of the products, recovery and reuse of palladium by alternative benign process are of prime importance. One such method exploits immobilization of palladium on solid support,⁵ and typical ligands employed for this purpose are phosphine, imine, acetylacetonate, and amine moieties. Among them, amine moieties are advantageous in tuning of their electronic characters, and its easy availability. From this point of view, various organic and inorganic solid supports bearing amine groups were developed for ligation with palladium.⁶

Cellulose has unlimited availability as a renewable agro-based resource and is biodegradable having interesting structure related properties with many commercial applications in various fields.⁷ The polymer is relatively inert to treatment with almost all com-

monly used solvents, because the hydroxyl groups, which are responsible for the majority of the reactions are involved in inter and intra-molecular hydrogen bonding. The properties of cellulose may be modified by changing both physical and chemical structure. Grafting onto cellulose is possible by growing polymer chain on active sites of the cellulose backbone. Surface hydroxyl groups of cellulose could be used to tether with the organofunctionalized alkoxy silane coupling reagents resulting in functionalized cellulose surfaces with C–O–Si bonds. However, this chemical bond can be easily hydrolyzed by water when the material is immersed in aqueous solution. Hence to make cellulose more reactive, surface modification has been carried out with metal oxides like cellulose– Al_2O_3 composite in which the aluminum oxide can be obtained highly dispersed on the surface with a good degree of adhesion.⁸ The use of silane coupling agents for surface modification is an important and well-established field,⁹ as these agents are useful for immobilizing specific chemical species on surfaces in organized monolayer assemblies. In the cellulose– Al_2O_3 composite, Al–OH groups present on the surface can easily react with Si–OMe groups of γ -aminopropyl trimethoxy silane (APTS) forming a very stable Al–O–Si bond with a high degree of organofunctionalization.

In continuation of our work associated in the direction of heterogeneous catalysis,¹⁰ the aim of the present study is to carry out synthesis and characterization of the amino groups attached palladium incorporated into hybrid cellulose– Al_2O_3 based $\text{Pd}@\text{Al}_2\text{O}_3\text{-CELL}$ catalyst (Fig. 1), which could function as heterogeneous catalyst for Suzuki–Miyaura cross coupling reaction having potentially high catalytic activity.

* Corresponding author. Tel.: +91 231 260 9240; fax: +91 231 269 2333.

E-mail address: rss234@rediffmail.com (R. Salunkhe).

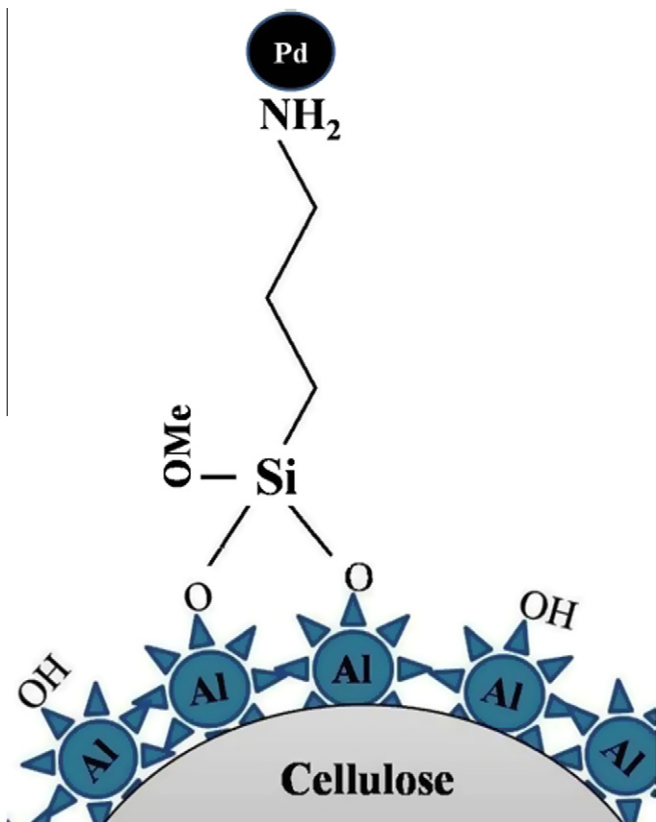
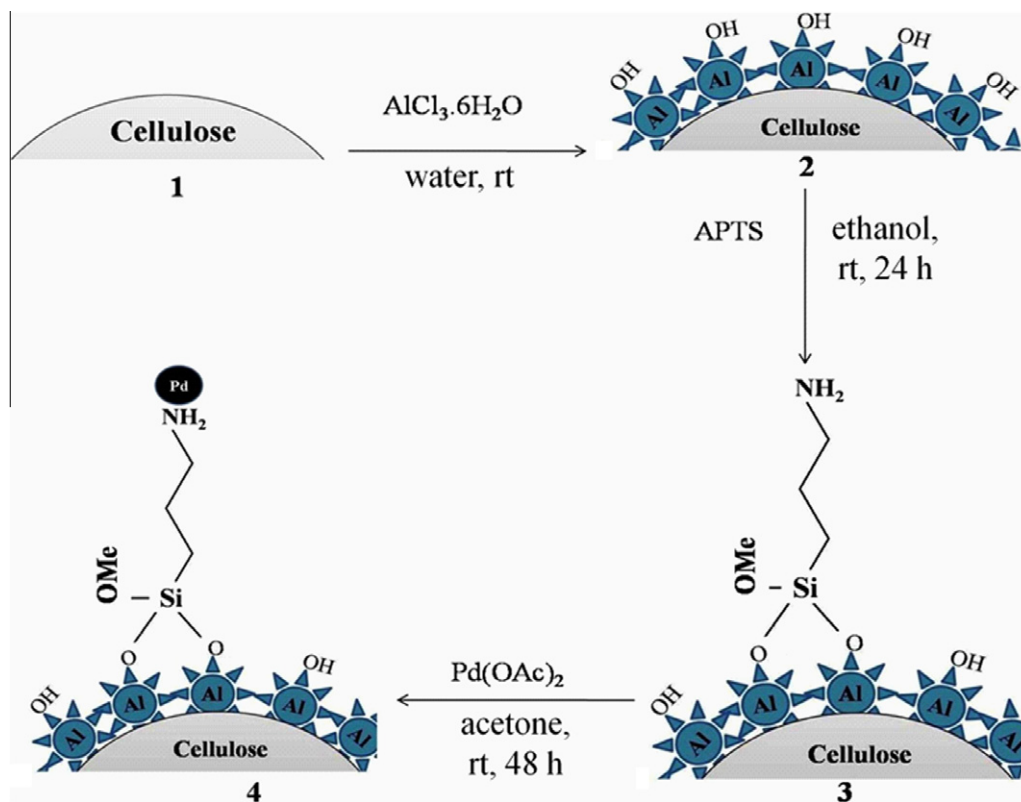


Figure 1. The conceptual illustration of Pd@Al₂O₃-CELL catalyst.

Synthesis of Pd@Al₂O₃-CELL catalyst **4** was achieved in a three step fashion as described in Scheme 1. The cellulose–aluminum oxide composite (Al₂O₃-CELL) **2**, and the experiment to modify **2** with γ -aminopropyl trimethoxy silane affording **3** was carried out as described in the literature.¹¹ The palladium was loaded on composite through the interaction of amino groups by slowly adding solution of palladium acetate in dry acetone¹⁸ and stirring the resulting suspension for 48 h at room temperature. The gray colored catalyst **4** (Pd@Al₂O₃-CELL) obtained was filtered, washed with dry acetone, and dried under vacuum at 25 °C for 8 h. The Pd content on **4** as determined by ICP-AES was suggested to be 0.070 mmol g⁻¹.

Our initial effort was focused on the characterization of the resulting solid material, which would be used as the heterogeneous catalyst in the Suzuki–Miyaura cross coupling reaction. A good adhesion is expected on composite, since the free aluminol groups, Al–OH on the alumina surface has a high affinity by the terminal silanol group of APTS.¹² The amount of aluminum was determined by calcining 0.300 g of **2** to 600 °C for 8 h and the residue weighed as Al₂O₃, which was found to be 3.27 wt %, corresponding to 0.31 mmol g⁻¹ aluminium, which was also supported by TGA analysis (3.44 wt %). The elemental analysis showed that, 0.56 mmol g⁻¹ of organic groups was attached on the **3**.

Thermal stability of the catalyst has a great effect on its catalytic activity and recyclability because the Suzuki–Miyaura coupling reaction is carried out under high temperature conditions. TGA–DSC profile (Fig. 2) of **4** indicated that the catalyst is stable up to 270 °C. Weight loss from 25 to 110 °C temperature was assigned to the loss of loosely bound water on the support (4.0%). The large weight loss of around 89% at temperature between 225 and 278 °C was due to the oxidative decomposition of polymer carrier. The sharp exothermic peak exhibited by DSC at the temperature



Scheme 1. Synthesis of Pd@Al₂O₃-CELL catalyst.

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