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Production of magnetically recoverable, thermally stable, bio-based catalyst: Remarkable turnover frequency and reusability in Suzuki coupling reaction

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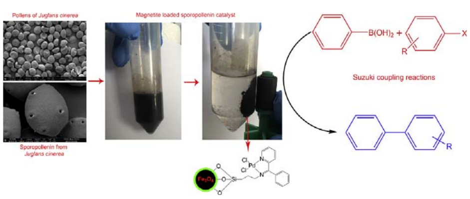
GRAPHICAL ABSTRACT



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ABSTRACT

In any catalysis system, regeneration of the used catalyst is of great importance to reduce the cost of industrial applications. However, recovery of the used catalyst from the reaction medium is a difficult task and this can hinder regeneration process. Magnetic separation has emerged as an effective tool to overcome the recovery problem. Hence, in this study a magnetically recoverable sporopollenin-based Pd catalyst has been designed and used in synthesis of biaryl compounds via Suzuki coupling reaction. The thermally stable catalyst exhibited excellent catalytic behaviour without giving any by-products. It is noteworthy that despite their low product yield of aryl chlorides in coupling reactions, remarkable product yields which are comparable to those of aryl bromides and iodides were recorded for aryl chlorides. With very low catalyst loading (1×10^{-3} mol%), the catalyst gave TOFs values exceeding one million; i.e., 1.237.500 in very short reaction time. Due to its magnetically separable nature, the catalyst could be recovered from the reaction media easily by increasing the reusability of the catalyst. Even in tenth run biphenyl yield dropped from 99 to 93%.

1. Introduction

Suzuki coupling reaction is an effective process in synthesis of organic compounds with broad range of functional groups through palladium-catalyzed carbon-carbon bond formation [1–5]. Various palladium catalyst systems have been tested in Suzuki coupling reactions and demonstrated that heterogeneous catalysts are advantageous over the homogeneous catalysts due to their ease of separation by conventional separation methods and elimination of toxic solvents [6,7]. Despite these properties, if the particle size is below (100 nm) or a very small amount of catalyst is used, catalyst loss can become inevitable when conventional separation methods are employed. Especially, recycle performance of the catalyst suffers from ineffective recovery of the used catalyst from the media, which is considered as an obstacle for up-scale industrial applications of the catalyst [8]. Recently, to overcome recovery problem of the used catalyst, various magnetically separable palladium catalysts have been produced and magnetic separation has emerged as an alternative to filtration [9]. This growing

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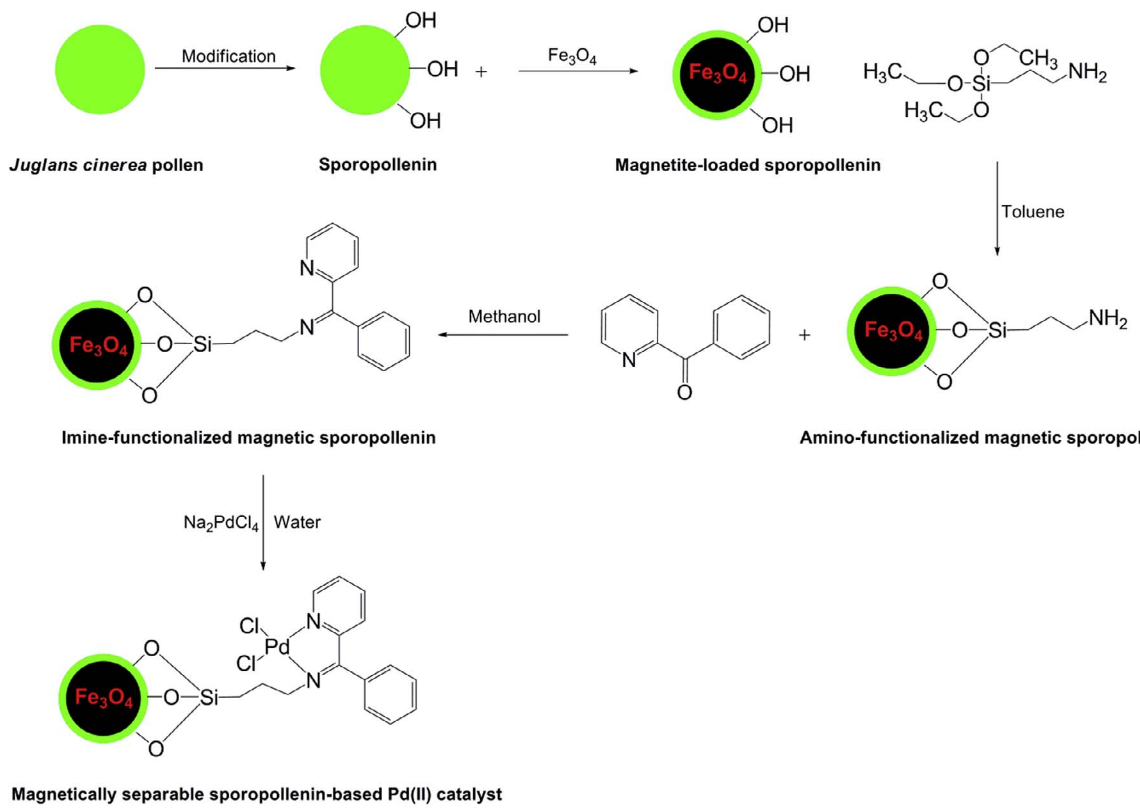

Scheme 1. Design of magnetically separable sporopollenin-based Pd(II) catalyst.

interest in immobilization of magnetite (Fe_3O_4, aka ferrite) into various palladium supports is not surprising to consider the superior properties of magnetite [10]. Magnetite particles have high surface area, paramagnetism and low toxicity, which makes them excellent candidates for stabilization of palladium catalyst [11]. Additionally, magnetite particles production is an easy and low-cost procedure [12], which is vital for commercialization of the catalyst. In literature many workers reported using nano/micro-sized magnetite particles as a catalyst support [9]. Despite the satisfactory catalytic performance, magnetite-loaded metal catalyst were not recovered from the reaction media in the original form when the catalyst was used in many cycles of the reactions requiring the use of harsh conditions [13]. However, immobilization of the magnetite particles onto the carriers proved to be highly effective in the stability of the catalyst [14]. In the last decade, various materials have been produced as support; polymeric micelles [15], silica particles [16], graphene [17]. On the other hand, bio-based materials are also emerging as an alternative to conventional materials in several fields including catalysis and energy [18–22]. Here, we have already an excellent candidate from the family of biopolymers; sporopollenin exine capsules. Due to their thermal, chemical and mechanical stability, they have been largely used in various applications [23]. Despite its excellent properties, sporopollenin exine capsules have been ignored by the researchers searching for stable catalyst supports. There is a large gap of information on the use of sporopollenin exine capsules as a catalyst support in the literature. In our previous study we extracted sporopollenin microcapsules from the pollens of *Betula pendula* (silver birch). Pd(II) loaded-*B. pendula* sporopollenin microcapsules produced high TONs (40.000) and TOFs 400.000) in Suzuki C—C coupling reactions [24]. However, we reported a decrease in the reusability performance of the catalyst due to not recovery problem of the catalyst after each run (8 runs).

White walnut *Juglans cinerea* L. is a short life tree [25] and it is commonly found in the area ranging from Eastern Europe to the Caucasus and Central Asia including the Baltic States, Belarus, Ukraine, Moscow, Smolensk and Kaluga regions [26]. White walnut is a wind pollinated species. Its flowering period depends on the location and happens from April to June. Pollen grain of *Juglans* spp. is relatively large and range from 30.3 to 42.6 μm in size depending on species. The grain might be triangular, rounded-triangular or circular [27]. The surface structure is polyporate with plenty circular micropores. Walnut pollen is shed in large quantities and can be collected easily. *J. cinerea* has been selected for the study due to the fact that it is common in Europe and almost over the world; it produces a lot of pollen which might be collected quite fast and easily in large quantities.

To enhance recycle performance of Pd catalyst and further increase its catalytic activity (for example TON, TOF and conversion yield), here we report design of a magnetically separable sporopollenin-based Pd(II) catalyst. We extracted the sporopollenin microcapsules from *J. cinerea* for the first time. Briefly, after the incorporation of magnetite particles into the sporopollenin micro carrier, we employed amine functionalisation through silylation procedure, which was followed by Schiff base formation to provide coordination sites for palladium ion. Pd(II) loaded-sporopollenin microcapsules were tested in synthesis of biaryl compounds in solvent-free media under microwave irradiation. The magnetically recoverable heterogeneous catalyst produced excellent TONs, TOFs and selectivity. Noticeably, magnetic separation facilitated the collection of the used catalyst and therefore we recorded high reusability for the catalyst. Also, when compared to aryl bromides and aryl iodides, coupling reactions of phenyl boronic acid with aryl chlorides suffer from low reactivity in cross-coupling reactions. The catalyst also produced a satisfactory performance in coupling reactions of aryl chlorides with phenyl boronic acid.

2. Material and methods

2.1. Materials

Sporopollenin used in the study was isolated from the pollens of *J.*

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